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METALLURGICAL CALCULATIONS

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METALLURGICAL CALCULATIONS

BY

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PART III.

THE METALS OTHER THAN IRON

(NON-FERROUS METALS.)

SECOND EDITION

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PREFACE TO SECOND EDITION.

The author has devoted considerable time to completing the chemical and physical data involved, so as to increase the usefulness of the work. In particular, where data are lacking the most probable approximation has been indicated, on the principle that it is better to make a guess and go ahead than to stop altogether. Practice has shown the value of thus making first approximations, and proceeding forthwith to the calculation of results which are valuable approximations, subject to further revision when more reliable data are forthcoming.

Criticism of methods, data or results will be very acceptable, as such kindly help will improve the accuracy of future editions.

JOSEPH W. RICHARDS.

PREFACE TO FIRST EDITION.

This volume constitutes the last of a set of three, published first as a serial in *Electrochemical and Metallurgical Industry*, from March, 1906 to July, 1908, and now presented in complete form. Part I is concerned with metallurgical principles in general, Part II with their special application to the problems arising in the iron and steel industry, and the present volume to their application in the metallurgy of metals other than iron. Being paged consecutively, they may, if desired, be bound together as one volume—which course is recommended to those making frequent use of the work.

The author concludes this arduous but intensely interesting task with the expression of many thanks to friends and friendly critics who have aided in perfecting the work. The flaws in the details have been many, due largely to the work being done under stress of numerous other duties, but it is hoped that the principles involved have in every case been clearly and correctly stated, and that the slips in details have affected but little the usefulness of the work as a whole.

In conclusion, the author takes this opportunity of expressing his gratification at the kindly reception accorded the work by the technical press, technical instructors in engineering schools, and particularly by practical men in the metal and other industries. These evidences of appreciation, spontaneous and in many cases totally unexpected, have been an intense gratification to the author.

JOSEPH W. RICHARDS

Lehigh University,
August, 1908.

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METALLURGICAL CALCULATIONS.

CHAPTER I.

THE METALLURGY OF COPPER.

Roasting and Smelting Copper Ores.

The facts with regard to the metallurgy of copper may be found in condensed form, very clearly stated, in Schnabel's "Handbook of Metallurgy," Vol. I; they may be found discussed at greater length in Dr. Peters' "Modern Copper Smelting" and "Principles of Copper Smelting," in Eissler's "Hydrometallurgy of Copper," and in Ulke's "Modern Electrolytic Copper Refining." *In the following presentation it will be possible to merely enumerate the different processes concerned, the principles embodied in each and the methods of calculating quantitatively the nature of the reactions involved.

The chief ore of copper is chalcopyrite, CuFeS_2 which contains when pure approximately 30 per cent iron and 35 per cent each of copper and sulphur. It is most frequently found mixed with silica, SiO_2 , as gangue, although various other gangue materials are sometimes present. This mineral is fusible, and if it were merely melted out of the enclosing rock, in an atmosphere which did not act upon it, it would simply lose one-fourth of its sulphur and melt to a fluid double sulphide of iron and copper, according to the following reaction:



The melted sulphide of copper and iron resulting is called "matte," and, in fact, any mixture of Cu_2S and FeS in any proportions is called matte, and in practice may contain small quantities of PbS , ZnS , BaS , NiS , As , Sb , Te and even of Fe_3O_4 , which is slightly soluble in these fused sulphides. In the majority of cases the matte is practically near enough to a mixture of Cu_2S and FeS to regard it as containing only those two substances.

*More recently, in Prof. H. O. Hofman's splendid treatise on "The Metallurgy of Copper."

Since the first operation in the extraction of copper from its usual sulphide ores is invariably the concentration to matte, we will first study the composition of this substance. Assuming matte to consist of Cu_2S and FeS in varying proportions, we may note that if it is all Cu_2S it contains $2 \times 63.6 = 127.2$ parts of copper to 32 parts of sulphur, or practically 4 copper to 1 sulphur, or is 80 per cent copper. For every 1.0 per cent of copper sulphide present there is, therefore, 0.8 per cent of copper in the matte; and, conversely, for every 1 per cent of copper in the matte there is 1.25 per cent of copper sulphide in it. The rest of the matte being iron sulphide, which contains 56 parts iron to 32 sulphur, it can be seen that the per cent of iron can be calculated for any per cent of copper; in fact, the per cent of copper fixes both that of iron and sulphur.

Illustration: A matte contains 40 per cent of copper. How much iron and sulphur does it contain? How much copper sulphide and iron sulphide?

$$\begin{aligned}
 40 \text{ per cent copper} &= 40 \times 5/4 = 50 \text{ per cent } \text{Cu}_2\text{S}. \\
 100 - 50 &= 50 \quad \text{“} \quad \text{FeS}. \\
 50 \text{ per cent FeS} &= 50 \times 56 \div 88 = 31.8 \quad \text{“} \quad \text{Fe}. \\
 100 - (40 + 31.8) &= 28.2 \quad \text{“} \quad \text{S}.
 \end{aligned}$$

We may generalize this solution and say that if X represents the percentage of copper in a matte, that the composition of the matte is as follows:

Per cent of copper	= X
Per cent of Cu_2S	= $1.25 X$
Per cent of FeS	= $100 - 1.25 X$
Per cent of $\text{Fe} = (100 - 1.25 X) 56/88$	= $63.6 - 0.795 X$
Per cent of $\text{S} = 100 - X - \text{Fe}$	= $36.4 - 0.205 X$

Similarly, if Y represents the percentage of iron in a matte its composition is:

Per cent of Fe	= Y
Per cent of FeS	= $1.57 Y$
Per cent of Cu_2S	= $100 - 1.57 Y$
Per cent of Cu	= $80 - 1.26 Y$
Per cent of S	= $20 + 0.26 Y$

Finally, if Z represents the percentage of sulphur in a matte its composition is:

Per cent of S	= Z
Per cent of Fe	= $3.89 Z - 77.8$
Per cent of Cu	= $177.8 - 4.89 Z$
Per cent of FeS	= $6.11 Z - 122.3$
Per cent of Cu ² S	= $222.3 - 6.11 Z$

The following tables may then be drawn up, and will be found useful for reference:

<i>Percentages.</i>				
<i>Cu.</i>	<i>Fe.</i>	<i>S.</i>	<i>Cu²S.</i>	<i>FeS.</i>
80	0.0	20.0	100.0	0.0
75	4.0	21.0	93.8	6.2
70	8.0	22.0	87.5	12.5
65	12.0	23.0	81.3	18.7
60	15.9	24.1	75.0	25.0
55	19.9	25.1	68.8	31.2
50	23.9	26.1	62.5	37.5
45	27.9	27.1	56.3	43.7
40	31.8	28.2	50.0	50.0
35	35.8	29.2	43.8	56.2
30	39.8	30.2	37.5	62.5
25	43.8	31.2	31.3	68.7
20	47.7	32.3	25.0	75.0
15	51.7	33.3	18.8	81.2
10	55.7	34.3	12.5	87.5
5	59.7	35.3	6.3	93.7
0	63.6	36.4	0.0	100.0

For regular use in a smelting works it is easy to calculate a table similar to the above for every one per cent of copper, and keep it under a glass cover for constant reference. Or, if preferred, a large piece of cross-section paper can be taken, and a diagram prepared with the percentages of copper as abscissas, from 0 to 80, and with ordinates running up to 100. A line drawn from an ordinate 36.4 at abscissa 0 to ordinate 20 on abscissa 80, will represent the sulphur content; a line from ordinate 63.6 on abscissa 0 to ordinate 0 on abscissa 80,

will represent the iron content; a line from 0 to ordinate 100 on abscissa 80 will represent the Cu^2S content; and a line from ordinate 100 on abscissa 0 to ordinate 0 on abscissa 80 will represent FeS content.

It has been already shown that if a chalcopryrite ore were smelted down, as in a shaft furnace, to a matte, that about a 35 per cent matte is as rich as could be made by simple fusion. In fact, a much poorer matte would usually result, because chalcopryrite is often accompanied by pyrite, FeS^2 , which on simple heating becomes FeS , and thus dilutes the matte still further.

Illustration: A chalcopryrite copper ore contains 30 per cent by weight of chalcopryrite and 25 per cent of iron pyrite. What grade of matte would result from a simple fusion of this ore, without roasting, in a reducing atmosphere?

Thirty per cent CuFeS^2 contains:

$30 \times 160 \div 368$	= 13 per cent Cu^2S .
$30 \times 176 \div 368$	= 14 " FeS .
25 per cent of FeS^2 will produce	
$25 \times 88 \div 120$	= 18 " FeS .
	—
Total matte = 45	" of the ore.

Composition of matte:

$$\begin{aligned}\text{Cu}^2\text{S} &= 29 \text{ per cent} = 23 \text{ per cent copper.} \\ \text{FeS} &= 71 \quad "\end{aligned}$$

It is thus seen that the presence of iron pyrites in the ore tends to lower the grade of the matte produced.

The essential principle of the metallurgy of copper is now before us. It is this fact: that if some of the sulphur in the ore be first removed by roasting, and this operation be followed by smelting, the copper will first take enough of the sulphur to form Cu^2S , and then what sulphur is left over will form FeS . The amount of FeS which will accompany the Cu^2S into the matte is entirely a question of how much sulphur is left to combine with iron after all the copper has been satisfied, and this amount of sulphur can be exactly controlled by the preliminary roasting.

Illustration: Taking the ore mentioned in the previous illustration, containing 30 per cent of chalcopryrite (= 10.4 per cent

of copper) and 25 per cent of iron pyrites, what per cent of sulphur does it contain, and what would be the quality of the matte produced by fusion in a reducing atmosphere if the sulphur were previously roasted down to $\frac{1}{2}$ or $\frac{1}{4}$ or $\frac{1}{8}$ of its original amount?

Sulphur in 30 per cent chalcopyrite:

$$30 \times 128 \div 368 = 10.5 \text{ per cent.}$$

Sulphur in 25 per cent pyrites:

$$25 \times 64 \div 120 = 13.3 \quad "$$

$$\text{Total} = 23.8 \quad "$$

If the sulphur were reduced to $\frac{1}{2}$, $\frac{1}{4}$ or $\frac{1}{8}$ its original amount there would remain, out of the 23.8 per cent, either 11.9, 5.95 or 2.97 parts of sulphur per 100 of original ore; i.e., per 10.4 parts of the copper. The 10.4 of copper requires 2.6 of sulphur to form Cu_2S , leaving the following amounts of sulphur in excess to form FeS :

Sulphur left in ore.....	11.90	5.95	2.97
Sulphur needed for Cu_2S	2.60	2.60	2.60
Sulphur left to form FeS	9.30	3.35	0.37
FeS which will be formed.....	25.61	9.21	1.02
Cu_2S formed.....	13.00	13.00	13.00
Matte formed.....	38.61	22.21	14.02
Per cent of Cu in matte.....	27.0	46.8	74.2

It is thus evident that the degree of the previous roasting determines absolutely the quality or grade of the matte formed on the subsequent smelting.

It can be readily seen that since partial roasting virtually oxidizes a portion or fraction of the ore, that it is the practical equivalent of roasting if we can get oxide ore to mix with sulphide ore. The raw oxide ore acts exactly as so much roasted ore, and thus enriches the matte on subsequent smelting.

Illustration: What proportion of a cuprite (copper oxide) ore, free from sulphur and containing 28 per cent of copper, can be mixed with the chalcopyrite ore of the previous illustrations, to produce a matte on subsequent reducing smelting containing 50 per cent of copper?

One hundred parts of the chalcopyrite ore contain 10.4 parts Cu, 20.8 parts Fe, 23.8 parts S.

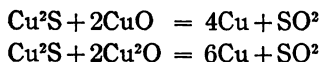
The sulphur, however, is not all available for making matte, because one-fourth of the sulphur in chalcopyrite and one-half that in pyrite is given off by simple heating. There would be lost, therefore, and not available for matte, sulphur as follows:

$$\begin{array}{rcl} \text{S in chalcopyrite} & 10.5 \times \frac{1}{4} & = 2.6 \text{ not available.} \\ \text{S in pyrite} & 13.3 \times \frac{1}{2} & = 6.7 \quad \quad \quad \text{“} \quad \quad \text{“} \\ & \hline & 9.3 & \quad \quad \quad \text{“} \quad \quad \text{“} \end{array}$$

Available sulphur = $23.8 - 9.3 = 14.5$ parts per 100 of ore.

In a 50 per cent matte there is (see previous table) 26.1 per cent of sulphur; 14.5 parts of sulphur available for matte is therefore capable of producing $14.5 \div 0.261 = 55.5$ parts of 50 per cent matte, which would contain 27.75 parts of copper. But there is only 10.4 of copper in the chalcopyrite ore, leaving therefore 16.35 of copper to be supplied by the cuprite ore, and therefore capable of taking up $16.35 \div 0.28 = 58$ parts of the oxide ore per 100 of the sulphide ore. A mixture of 100 of the sulphide ore and 58 parts of the oxide ore would therefore smelt down in a reducing atmosphere to a 50 per cent matte.

We have carefully specified a reducing atmosphere as the condition for smelting down to produce the calculated results, because under these conditions the oxygen of the roasted ore or of the raw oxide ore added cannot combine with the sulphur of the ore and go off as SO^2 , but is taken up by the carbon or CO in the smelting furnace. In smelting in a shaft furnace with carbon as fuel these conditions exist, and the sulphur in the charge can be counted on as practically all forming matte. If the smelting is done in a reverberatory furnace, with a neutral atmosphere, much sulphur will be removed from the charge by the oxygen of the roasted ore or of the raw ore added, and a richer matte results. The reactions of this elimination of sulphur are mostly



On an average, a matte 10 per cent richer in copper will be obtained from a given roasted ore by smelting it down in a reverberatory furnace, where these reactions between sulphide

and oxide of copper can occur, than in shaft furnace smelting with coke, in which the oxygen of the charge is taken up by the carbon.

There is a third variety of smelting which is in reality a combined roasting and smelting-down operation. We refer to what is called pyritic smelting, where a sulphide ore is roasted in a blast of air so rapidly that the heat generated melts down the charge and produces a concentrated matte. This operation is done on pure sulphides, however, without preliminary roasting, and will be subsequently discussed by itself.

The Roasting Operation.

When an ore is roasted it loses some sulphur and takes up oxygen. The roasted ore will therefore have a different weight from the unroasted ore. Thus:

100 parts of Cu^2S become	90.0 parts of Cu^2O .
100 parts of Cu^2S become	100.0 " CuO .
100 parts of Cu^2S become	{ 100.0 " CuSO^4
	{ 50.0 " CuO .
100 parts of FeS^2 become	64.5 " Fe^3O^4
100 parts of FeS^2 become	66.7 " Fe^2O^3
100 parts of FeS^2 become	126.7 " FeSO^4

Problem 101.

A pyritous copper ore from Ely, Vt. (see Peters' "Modern Copper Smelting," p. 133), contained before and after roasting, in percentages:

	<i>Before.</i>	<i>After.</i>
Sulphur.....	32.6	7.4
Copper.....	8.2	9.1

The condition of the copper in the roasted sample was determined as

	<i>Per Cent</i>
Copper as CuSO^4	1.3
Copper as CuO	2.1
Copper as Cu^2S	5.7

Required:

- (1) The weight of roasted ore per 100 of raw ore.
- (2) The proportion of the sulphur removed by roasting.

(3) The grade of matte which would be formed by smelting down in a reducing atmosphere in a shaft furnace..

(4) The grade of matte which would be formed by smelting down in a neutral atmosphere in a reverberatory furnace.

Solution:

(1) Since no copper is lost, there will be produced per 100 of raw ore:

$$100 \times \frac{8.2}{9.1} = 90.1 \text{ of roasted ore.} \quad (1)$$

	<i>Parts.</i>
(2) Sulphur in 100 of raw ore	= 32.6
Sulphur in 90.1 of roasted ore = 90.1×0.074	= 6.7
Sulphur eliminated	<u>= 25.9</u>

Proportion removed:

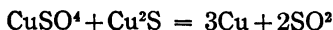
$$\frac{25.9}{32.6} = 0.794 = 79.4 \text{ per cent.} \quad (2)$$

(3) Per 100 of roasted ore we have:

	<i>Kg.</i>
Sulphur to form $\text{Cu}_2\text{S} = 9.1 \times 0.25$	= 2.3
Sulphur to form $\text{FeS} = 7.4 - 2.3$	= 5.1
FeS formed = $5.1 \times 88/32$	= 14.0
Cu_2S	<u>= 11.4</u>
Matte formed	= 25.4

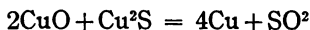
$$\text{Per cent of copper} = \frac{9.1}{25.4} = 0.358 = 35.8 \text{ per cent.} \quad (3)$$

(4) In



every 1 part of copper as CuSO_4 reduces two parts of copper as Cu_2S , and causes the elimination as gas of 1 part of sulphur.

In



1 part of copper as CuO reduces 1 part of copper as Cu_2S , and

causes the elimination of one-fourth its weight of sulphur. Therefore, the sulphur eliminated by the reactions given is:

	<i>Parts.</i>
By reaction of sulphate on sulphide 1.3×1	= 1.3
By reaction of oxide on sulphide $2.1 \times \frac{1}{4}$	= 0.5
	<hr/>
Total =	1.8
Sulphur remaining to form matte = $7.4 - 1.8$	= 5.6
Sulphur needed to form Cu_2S	= 2.3
Sulphur left to form FeS = $5.6 - 2.3$	= 3.3
FeS formed = $3.3 \times 88/32$	= 9.1
Cu_2S formed	= 11.4
	<hr/>
Matte formed	= 20.5

$$\text{Per cent of copper} = \frac{9.1}{20.5} = 0.444 = 44.4 \text{ per cent.} \quad (4)$$

In the roasting of ores a large amount of heat is set free, since both the sulphur and the metal are usually oxidized.

Problem 102.

In the ore of Problem 101, taking the data given for its weight before and after roasting, how much heat was generated in its roasting per kilogram of ore treated.

Solution: Starting with 100 parts of original ore it contained 32.6 parts of sulphur and 8.2 of copper. The latter corresponds to 2.05 of sulphur as Cu_2S , which would mean 8.2 of sulphur altogether as chalcopyrite, leaving 24.4 of sulphur present in the ore as iron pyrites.

In 100 parts of roasted ore we have 5.7 parts of copper as Cu_2S , therefore unchanged, 2.1 parts changed to CuO and 1.3 parts changed to CuSO_4 . These contain sulphur as follows:

	<i>Parts.</i>
Sulphur for 5.7 Cu as Cu_2S	= 1.4
Sulphur for 1.3 Cu as CuSO_4	= 0.7
	<hr/>
Sulphur for copper compounds	= 2.1
Sulphur for FeS = $7.4 - 2.1$	= 5.3
FeS = $5.3 \times 88/32$	= 14.6

Per 90.1 of roasted ore there is present:

Cu as CuSO^4	= 1.17
Cu as Cu^2S	= 5.14
Cu as CuO	= 1.89
Fe as $\text{FeS} = 9.3 \times .901$	= 8.38
Sulphur	= 6.67

We therefore have:

Heat to Decompose Raw Ore.

		<i>Calories.</i>
8.20 Cu as Cu^2S	= 8.20×160	= 1,312
18.85 Fe as sulphide	= 18.85×429	= 8,087
		<hr/>
	Sum =	9,399

Heat of Formation of Products.

5.14 Cu as Cu^2S	= 5.14×160	= 822
1.17 Cu as CuSO^4	= $1.17 \times 2,857$	= 3,343
1.89 Cu as CuO	= 1.89×593	= 1,121
25.93 S to SO^2	= $25.93 \times 2,164$	= 56,112
9.55 Fe to Fe^2O^4	= $9.55 \times 1,612$	= 15,395
9.30 Fe to FeS	= 9.30×429	= 3,990
		<hr/>
	Sum =	80,783

Net heat evolved = $80,783 - 9,399 = 71,384$ Calories.

Per 1 kg. of ore = 713 "

In the roasting of copper ore the heat generated by the oxidation of the ore is an important item in the heat required by the furnace. In the above case, for instance, each kilogram of ore developed about one-tenth as much heat as a kilogram of coke, and with proper arrangements for conserving heat, such as thick walls and compact shape of furnace, combined with regeneration of heat from the cooling ore, there is no reason why such an ore should not be made to roast itself. Such a scheme, when practicable, is highly economical in districts where fuel is dear. A long-bedded calciner, with its single hearth and large radiating surface, cannot meet these conditions, but furnaces having superposed hearths and arrangements for discharging cold ore, cooled by the incoming air, such as the Spence and MacDougal furnaces, can work on many ores without using other fuel.

Problem 103.

An improved Spence furnace used at Butte, Mont., calcines 90,000 pounds of concentrates in 24 hours, of the following composition:

	<i>Per Cent.</i>
Copper.....	9.8
Iron.....	33.8
Silica.....	13.3
Sulphur.....	41.2

Four-fifths of the sulphur is removed, and the roasted ore is practically discharged cold; 1,500 pounds of slack coal, caloric power 6,500, is used per day. The furnace gases contain:

	<i>Per Cent.</i>
CO ²	0.6
SO ²	7.2
H ² O.....	0.6
N ²	81.3
O ²	10.3
	<hr/> 100.0

and escape into the chimney at 200° C. Ore charged and discharged cold. Furnace has an outside radiating surface of 5,000 square feet.

Required:

- (1) The heat balance sheet of the furnace.
- (2) The proportion of the heat generated by the roasting of the ore and by the combustion of fuel.
- (3) The heat radiated and conducted to the air per square foot of outside surface per minute.

Solution:

(1) Per 100 of ore used the unroasted and roasted ore will contain, respectively:

Copper.....	9.8	9.8
Iron.....	33.8	33.8
Silica.....	13.3	13.3
Sulphur.....	41.2	8.2

Assuming that the copper remains in the roasted ore, two-thirds as Cu²S, one-quarter as CuO and one-tenth as CuSO⁴, while the iron takes the rest of the sulphur to form FeS, the ex-

cess of iron forming half Fe^2O^3 and half Fe^3O^4 . We have the composition of the roasted ore as:

Cu^2S	8.2
CuO	3.1 ✓
CuSO^4	2.0 ✓ 2.5
FeS	17.0
Fe^2O^3	16.4 ✓
Fe^3O^4	15.9 ✓
SiO^2	13.3
	<hr/> 75.9

The copper and iron existed in the unroasted ore virtually as Cu^2S , FeS and FeS^2 , and therefore the 8.2 of Cu^2S and the 17.0 of FeS in the roasted ore can be considered as unchanged. The actual change in the roasting has been the formation of 3.1 CuO and 2.0 CuSO^4 from Cu^2S , and the formation of 16.4 Fe^2O^3 and 15.9 Fe^3O^4 from FeS . If we, therefore, subtract from the heat of formation of these amounts of CuO , CuSO^4 , Fe^2O^3 and Fe^3O^4 , and the SO^2 formed, the heat required to resolve the Cu^2S , FeS and FeS^2 into their constituents, we shall get the net heat evolution in the roasting process. The heats of formation involved are:

Molecular Heat.

(Cu^2, S)	=	20,300	Calories	=	127	Cal. per	of product.
(Cu, O)	=	37,700	"	=	471	"	"
$(\text{Cu}, \text{S}, \text{O}^4)$	=	181,700	"	=	1,136	"	"
(Fe, S)	=	24,000	"	=	273	"	"
$(\text{Fe}^2, \text{O}^3)$	=	195,600	"	=	1,223	"	"
$(\text{Fe}^3, \text{O}^4)$	=	270,800	"	=	1,167	"	"
(S, O^2)	=	69,260	"	=	1,082	"	"

We then have the heat evolved and absorbed as follows:

	<i>Evolved.</i>	<i>Calories.</i>
Formation of CuO	3.1×471	= 1,460
Formation of CuSO^4	$2.0 \times 1,136$	= 2,272
Formation of Fe^2O^3	$16.4 \times 1,223$	= 20,057
Formation of Fe^3O^4	$15.9 \times 1,167$	= 18,555
Formation of SO^2	$66.0 \times 1,082$	= 71,412
	<hr/>	
Total		= 113,756

Absorbed.

Decomposition of Cu_2S	$4.1 \times 127 =$	521
Decomposition of FeS	$36.1 \times 273 =$	9,855
Total =		10,376

Net heat evolution per 100 of concentrates:

$$113,756 - 10,376 = 103,380 \text{ Calories.}$$

The gases contain 33 pounds of sulphur for every 100 of ore roasted, and the analysis shows there is 0.072 cubic foot of SO_2 in each cubic foot of chimney gas. This weighs $0.072 \times 2.88 = 0.2074$ ounces, and contains just half its weight = 0.1037 ounces = 0.00674 pounds of sulphur. There is therefore produced, per 100 pounds of ore, $33 \div 0.00674 = 4,896$ cubic feet of chimney gas.

This contains, from its analysis:

CO_2	29	cub. ft.
SO_2	353	" "
H_2O	29	" "
O_2	504	" "
N_2	3,981	" "

and at 200°C . carries heat up the chimney as follows:

$S_m (0 - 200^\circ)$			
CO_2	$29 \times 0.414 =$	12 oz. cal. per 1°	
SO_2	$353 \times 0.420 =$	148	" "
H_2O	$29 \times 0.370 =$	11	" "
$\text{O}_2 \}$	$4,485 \times 0.308 =$	1,381	" "
$\text{N}_2 \}$			
	Sum =	1,552	" "
		=	97 lb. Cal. per 1° .
			= 19,400 lb. Cal. per 200° .

The fuel evolves $6,500 \times 1,500 = 9,750,000$ pound Calories per day = 10,830 pound Calories per 100 of ore roasted.

(1) BALANCE SHEET PER 100 OF ORE ROASTED.

Lb. Calories.

Evolved by the fuel.....	10,830
Evolved by the roasting operation.....	103,380

Sum 114,210

Loss in chimney gases.....	19,400
Loss by radiation and conduction.....	94,810
	<hr/>
Sum	114,210

(2) The proportion of the total heat generated by the ore itself is:

$$\frac{103,380}{114,210} = 0.90 = 90 \text{ per cent.}$$

by the fuel 10 “

The heat lost by radiation and conduction per day is:

	<i>Lb. Calories.</i>	
$94,810 \times 900$	=	85,329,000
Per minute	=	59,000
Loss per square foot of surface per		
minute = $\frac{59,000}{5,000}$	=	11.8 (3)

Problem 104.

The Evans-Klepetko cylindrical roaster used at Butte, Mont., is 19 feet high, 18 feet in diameter, and roasts 80,000 pounds of concentrates daily from 35 per cent sulphur down to 7 per cent (Dr. Peters). The evolution of heat in the roasting operation is sufficient to supply all the heat needed. The stirrer arms are cooled by water circulation, 100 pounds of water being used per minute, and raised in temperature 50° C. Assume the evolution of heat to be 90 per cent as great as in the roasting of ore in Problem 103, and the chimney loss to be correspondingly smaller.

Required:

- (1) The heat balance sheet per 100 of ore roasted.
- (2) The loss by radiation and conduction per square foot of outside surface of the furnace.

Solution:

(1)	<i>Heat Evolved.</i>	<i>Lb. Calories.</i>
90 per cent of 103,380		= 93,040

Heat Distribution.

Heat in chimney gases	= 17,460
Heat in cooling water	= 9,000
Heat lost by radiation and conduction	= 66,580
Sum	= 93,040 (1)

(2) The outside surface consists of the top and bottom and sides. Their area is as follows:

	<i>Sq. Feet.</i>
Sides $18 \times 3.14 \times 19$	= 1,074
Bottom $18 \times 18 \times 0.78$	= 253
Top	= 253
Total	= 1,580
Loss by radiation and conduction	<i>Lb. Calories.</i>
Per 100 of ore	= 66,580
Per day	= 53,264,000
Per minute	= 37,000
Per square foot surface per minute	
	$= \frac{37,000}{1,580} = 23.4$ (2)

It is interesting to note, as comparing this compact cylindrical furnace with the rectangular furnace of Problem 103, that although no fuel is used and cooling water is used, and radiation losses per square foot are greater because of thinner walls, yet the much smaller radiating surface more than counter-balanced these considerations, and permitted the furnace to run more economically.

Thick walls and minimum radiating surface are the requisites for economy of fuel in general, and the *sine qua non* for roasting copper sulphide ores by their own self-generated heat of oxidation.

Pyritic Smelting.

This method of smelting is sometimes called pyrite smelting, because usually practiced on ores rich in pyrite; it is, however, just as applicable to ores rich in pyrrhotite (magnetic pyrites) or chalcopyrite (copper pyrites), and therefore the more general term *pyritic* smelting is really more proper and descriptive of the range of process.

For a full description of pyritic smelting we would refer the reader to the volume "Pyrite Smelting,"¹ a symposium of information contributed by nearly forty metallurgists, and edited by T. A. Rickard, or to Sticht's monograph, "Ueber das Wesen des Pyrit Schmelzverfahrens,"² or to Dr. Peters' "Principles of Copper Smelting,"³ which contains a 125-page chapter upon it.

A brief statement of the principles of the process is as follows: Given an ore containing considerable silica in the free state and a good percentage of pyrite, pyrrhotite or chalcopyrite, it is possible to smelt it down in a shaft furnace to a ferrous silicate slag and a matte by means of cold blast and without using any carbonaceous fuel. Whether fuel is cheap or dear the possibility of dispensing with it when smelting down certain sulphide ores is highly important; yet it is only within a very few years that the principles involved have been well enough understood to make the process a recognized success. As far as the *modus operandi* is concerned, the ore is charged into a shaft furnace, water-jacketed at the boshes and smelting zone, with enough flux to furnish 10 to 20 per cent of CaO or similar alkaline earth base to the slag, and a high pressure of blast is employed, such as would correspond to a high rate of driving in ordinary smelting (up to $3\frac{1}{2}$ pounds pressure per square inch is used). The matte and slag either collect in the well of the furnace or run continuously into an external settler, where they separate as in ordinary smelting. The heat necessary to run the furnace is all supplied by the oxidation of sulphur and iron in the furnace, the former escaping as SO_2 in the gases and the latter as silicate of FeO in the slag. The process may be regarded as a very quick partial roasting of the ore, accompanied by simultaneous formation of melted slag and matte, because of the high temperature generated by the oxidation itself.

There is hardly any process in the whole of metallurgy which invites so strongly to quantitative calculations, such as we are endeavoring to encourage in this treatise; and there are fewer processes which present such a lack of data upon which to base the calculations. Not only are the physical and chemical (thermochemical) data scarce, but the ordinary industrial

1 *Engineering and Mining Journal*, New York, 1905.

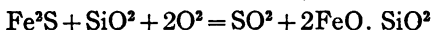
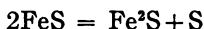
2 Wilhelm Knapp, Halle, 1906. Reprinted from "Metallurgie."

3 Hill Publishing Company, New York, 1907.

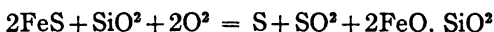
data, careful details of the running of the furnaces, weights and compositions of charges and products, analyses and temperature of gases, are very largely lacking—most that we have of value are those furnished as recently as 1906 by Robert Sticht, director of the Mount Lyell furnaces in Tasmania, and these apply only to his particular furnaces and operations.

FUNDAMENTAL PRINCIPLES.

Taking the simplest case, and supposing FeS^2 and SiO^2 to be charged into a pyritic smelting furnace, we know without a doubt that the FeS^2 becomes approximately FeS at a red heat, and the sulphur thus evolved is driven off at a part of the furnace where there is no free oxygen, so remains in the furnace gases as sulphur vapor. At a temperature of 1400° Sticht has shown experimentally that the FeS becomes something like Fe^2S^5 , and it is known that the sulphur in the matte is often less than can correspond to FeS . But the actual temperature of combustion attained at the moment of oxidation in pyritic smelting is higher even than $1,400^\circ$, and it is almost certain that as FeS oxidizes, it is heated so intensely that it really goes through two stages, first decomposing to Fe^2S and then oxidizing to FeO :



or, putting it all together:



If we cast up the thermochemistry of this reaction we find a very considerable evolution of heat, easily comparable with the heat of oxidation of carbon, and accounting for the running of the furnace. The thermochemical analysis of the above reaction is:

	<i>Absorbed.</i>	<i>Calories.</i>
Decomposition of 2FeS		48,000
	<i>Evolved.</i>	
Formation of 2FeO	=	131,400
“ “ SO^2	=	69,260
“ “ $2\text{FeO} \cdot \text{SiO}^2$	=	8,900
		<hr/> 209,560
Excess of heat evolved	=	161,560

131,400
69,260
8,900
209,560
161,560

The FeS and SiO² come into the zone of oxidation already heated to a high temperature by their contact with the rising hot gases. They come to this zone, or focus, heated to at least 1,000°, and perhaps hotter, before they begin themselves to oxidize. The air comes in cool, and we will not credit it with any sensible heat at the moment oxidation begins.

THEORETICAL TEMPERATURE AT THE FOCUS.

With these data, and a few reasonable assumptions, we can calculate how hot the focus will become at its hottest point. This calculation is similar to that for the calorific intensity of combustion of a fuel, or the theoretical temperature before the tuyeres of a blast furnace. Making the calculation for the quantities represented by the equation, and assuming

Heat in FeS at 1000° melted	200	Calories
" " SiO ² at 1000° solid	260	"
" " Slag ($\frac{5}{3}$ weight of FeO): $0.27(t - 1100) + 300$		"
" " Matte ($\frac{1}{3}$ weight of slag): $0.14(t - 1000) + 200$		"

we can calculate the theoretical temperature t , to which the slag, matte and gases will be raised by the heat at hand, which latter is the sensible heat in FeS and SiO² at, say, 1,000°, plus the heat evolved in the reaction, plus sensible heat in matte at 1000°:

	<i>Calories.</i>
Heat in 2FeS at 1000°: 176×200	= 35,200
" " SiO ² at 1000°: 60×260	= 15,600
" of the reaction	= 161,560
" in matte: 80×200	= 16,000

Total heat available = 228,360

Calorific capacity of the products:

SO ²	= $22.22(0.36t + 0.0003t^2)$
N ²	= $170(0.303t + 0.000027t^2)$
Slag	= $240[300 + (t - 1100) 0.27]$
Matte	= $80[200 + (t - 1000) 0.14]$

$$\text{Sum} = 0.0113t^2 + 135.5t + 5,520 = 228,360$$

Whence $t = 1465^\circ\text{C.}$

The result of our calculation is to show that a temperature sufficient to run the furnace is theoretically obtainable if the weight of slag made, carrying a given weight of FeO, is not too great. Supposing the silica and other slag-forming ingredients are so heavy in comparison to the amount of FeO formed by oxidation that the slag contains only 50 per cent of such FeO, then the weight of slag above would be 288 instead of 240, and the temperature attained only 1,365° instead of 1,465°. This reduction, however, is getting perilously near the temperature necessary to keep the furnace in operation. The formation temperatures of copper blast-furnace slags are 1,100° to 1,200°, and an over-heating of at least 50° is necessary, for practical operation of the furnace. Suppose we put 1,200° as the minimum theoretical temperature which will run the furnace, then the maximum weight of slag can be calculated in the above solution for t , and thence the minimum percentage of FeO.

Let X be the maximum weight of slag, for t a minimum of 1,200°. Then we have:

	Calories.
Heat in SO_2 at 1200°	= 19,248
" " N_2 at 1200°	= 68,422
" " Slag at 1200°	= 330 X
" " Matte at 1200°	= 18,240
Whence	105,940 + 330 X = 228,360
and	X = 371 kg.

Since this maximum weight of slag must contain the 2FeO = 144 kg. of FeO, the minimum percentage of FeO produced by oxidation and going into slag in pure pyritic smelting, must be

$$144 \div 371 = 0.39 = 39 \text{ per cent.}$$

The margin for working pyritic smelting is ordinarily so small that variations of the temperature of the blast and its humidity must exercise a large influence in the running of the furnace. This coincides with experience as far as the heating of the blast is concerned. At La Lustre Smelter, Santa Maria del Oro, Mr. Koch says that "a warm blast of 200° C. is a *sine qua non* with us; it spelled success; cold blast meant failure." This is, however, an extreme position; many other metallurgists working other ores have run entirely with cold blast, but there

is no doubt that smelting is easier, faster and more regular when using warm blast. No one has yet tried drying the blast, but there can be no doubt that under some circumstances this would contribute greatly to the regularity of running and would increase the theoretical temperature obtainable at the focus or smelting zone.

USE OF AUXILIARY COKE.

When the amount of slag-forming material in the charges is high, pyritic smelting using cold, ordinary blast may become impossible for lack of sufficient calories to melt the slag and matte. In this case, which often occurs, some coke may be used, the combustion of which to CO^2 at the focus increases materially the heat available and the temperature. If the temperature desired is, let us say, $1,400^\circ$, carbon at $1,000^\circ$ can burn to CO^2 , yielding CO^2 and N^2 as products, and give a large surplus of heat to the charge at this temperature.

One kilogram of coke, containing 0.9 kg. of carbon, will form 3.3 kg. of CO^2 (1.67 cubic meters) and 6.35 cubic meters of N^2 . The heat generated is 7,290, and adding in the heat in hot carbon at $1,000^\circ$ (342) we have 7,632 Calories generated. But in the products at $1,400^\circ$ we have:

	<i>Calories.</i>
CO^2 1.67 [0.37 + 0.00022 (1400)] \times 1400	= 1582
N^2 6.35 [0.303 + 0.000027 (1400)] \times 1400	= 3038
	<hr style="width: 10%; margin: 0 auto;"/> 4620

Surplus, to help the fusion

$$7632 - 4620 = 3012 \text{ Calories.}$$

Each kilogram of coke used will therefore melt down, at 1400° ,

$$3012 \div 330 = 9 \text{ kg.}$$

of slag, and thus relieves the situation materially. At Mount Lyell, 0.5, 1.0 and 1.5 per cent of coke (reckoned on the charge) is found necessary, according to the nature of the ore worked. From this we have increasing quantities of coke used up to several per cent, according to the exigencies of the case, and we pass by insensible gradations through partial pyritic smelting to ordinary smelting. As the carbon is increased the sulphides get less and less of the oxygen blown in, and therefore the degree of oxidation of sulphides is lower and the concentra-

tion poorer. The best concentration, using unroasted sulphide ore, is obtained by pure pyritic smelting, if there are enough sulphides present to generate the requisite heat and temperature.

RATE OF SMELTING.

In all that precedes it has been assumed that the furnace was driven fast enough. Other things being equal, the harder a furnace is blown the more material can be put through it, and the smaller the heat losses by radiation and conduction when expressed per unit of charge treated or of product obtained. It is, therefore, possible to increase the temperature in the focus simply by harder blowing, and thus to decrease the amount of auxiliary coke needed. A similar effect is produced by heightening the furnace shaft, since this increases the regeneration of heat by the charges, they coming to the hot zone more intensely preheated by the ascending gases. The present tendency in pyritic smelting is undoubtedly to increase the rate of driving, heighten the furnace, and thus decrease the auxiliary coke needed and dispense with hot blast, which is somewhat of a complication.

The possibility of smelting in any manner depends on being able to generate the theoretical temperature necessary for running the furnace, and then keeping the rate of smelting per minute per unit area of the smelting zone as high as practicable. This achieves two practical results, viz.: makes the actual temperature of melted-down slag and matte approximate closer to the theoretical temperature of the focus, and gets the largest tonnage through the furnace. As we gradually increase the smelting rate we increase the temperature of the focus, because of decreased radiation losses; but, on the other hand, we tend to decrease the relative amount of oxidation, because of the decreased time that the charge is subjected to oxidation; there must be a certain rate of driving which will attain the maximum of oxidation, *i.e.*, of concentration, and past which increased tonnage is put through at the cost of decreased concentration.

Problem 105.

W. H. Freeland (*Engineering and Mining Journal*, May 2, 1903), at Isabella, Tenn., smelted Ducktown pyrrhotite ore in a water-jacketed Herreshoff furnace, having a cross-sectional

area at the tuyeres of 21.7 square feet. The analyses of the materials used and the products are as follows:

<i>Charges.</i>				
	<i>Ore.</i>	<i>Quartz.</i>	<i>Slag.</i>	<i>Coke.</i>
Cu.....	2.744	0.73
Fe.....	36.519	1.45	39.20	2.30
S.....	24.848	0.32	1.75	1.58
SiO ²	18.548	96.79	30.90	8.41
CaO.....	7.294	0.23	8.51
MgO.....	2.672	2.71
Zn.....	2.556	2.88
Al ² O ³	0.911	0.32	1.90	3.56
Mn.....	0.770	0.85
O.....	0.38	11.37	1.00
C.....	83.86
CO ²	3.138
Loss.....	0.39

<i>Products.</i>			
	<i>Matte.</i>	<i>Flue Dust.</i>	<i>Slag.</i>
Cu.....	20.00	2.20	0.37
Fe.....	47.15	30.80	38.84
S.....	24.00	16.51	1.74
SiO ²	0.44	23.92	32.60
CaO.....	0.10	4.45	8.24
MgO.....	1.38	3.44
Zn.....	2.05	2.98	1.54
Al ² O ³	0.82	1.94	1.50
Mn.....	0.53	0.15	0.80
O.....	4.91	15.26	10.88

The charges and products per 24 hours and per 1,000 pounds of ore used were

Charges:

Ore.....	68.0 tons	1000 lbs.
Quartz.....	5.4 "	80 "
Slag.....	9.8 "	145 "
Coke.....	2.3 "	34 "

Products:

Matte.....	8.34 tons	122.65 lbs.
Flue dust.....	1.75 "	25.71 "
Slag.....	63.81 "	938.24 "

Blast applied, 4,500 cubic feet displacement per minute, at 17-ounce pressure. Assume temperature of gases 450° C., and that they contain no CO, SO^2 or free O^2 (no analyses are given). Assume matte and slag issuing from the furnace at $1,300^{\circ}$ (no temperature given).

Required:

- (1) A balance sheet of everything entering and leaving the furnace.
- (2) The volume efficiency of the blowing plant.
- (3) The heat generated per minute, per square foot of cross-section, in the focus of the furnace.
- (4) The theoretical temperature at the focus.
- (5) The proportion of the heat generated in the focus by the combustion of carbon and by the oxidation of sulphides.
- (6) If hot blast were used what should be its temperature to be able to dispense with the coke charged? Assume that the pressure was increased so as to keep the delivery to the furnace constant per minute.

Per 1000 of Ore Smelted.

<i>Charges.</i>		<i>Matte.</i>	<i>Flue Dust.</i>	<i>Slag.</i>	<i>Gases.</i>
Ore (1000).					
Cu.....	27.44	24.53	0.57	2.34
Fe.....	365.19	57.83	7.92	299.44
S.....	248.48	29.44	4.24	16.33	98.47
SiO^2	185.48	0.54	6.15	178.79
CaO.....	72.94	0.12	1.14	71.68
MgO.....	26.72	0.35	26.37
Zn.....	25.56	2.51	0.77	22.28
Al^2O^3	9.11	1.00	0.50	7.61
Mn.....	7.70	0.64	0.14	6.92
CO^2	31.38	31.38

Quartz (80).

Fe.....	1.16	1.16
S.....	0.26	0.26
SiO^2	77.43	77.43
CaO.....	0.18	0.18
Al^2O^3	0.26	0.26
H^2O	0.71	0.71

<i>Charges.</i>		<i>Matte.</i>	<i>Flue Dust.</i>	<i>Slag.</i>	<i>Gases.</i>
Slags (145).					
Cu.....	1.06	1.06
Fe.....	56.84	56.84
S.....	2.54	2.54
SiO ²	44.81	44.81
CaO.....	12.34	12.34
MgO.....	3.93	3.93
Zn.....	4.18	4.18
Al ² O ³	2.76	2.76
Mn.....	1.23	1.23
O.....	15.31	6.04	3.93	5.34
Coke (34).					
Fe.....	0.78	0.78
S.....	0.54	0.54
SiO ²	2.86	2.86
C.....	28.51	28.51
Al ² O ³	1.21	1.21
O.....	0.10	0.10
Blast (1,191).					
O ²	274.91	97.92	176.99
N ²	916.37	916.37
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
	2450	122.65	25.71	946.16	1355.77

Notes on the Balance Sheet.

The oxygen of the blast goes as SO² and CO² into the gases and as oxides into the slag. The amount required for the gases is

$$\text{O in SO}^2 = \text{S} \times \frac{32}{32} = 100.96$$

$$\text{O in CO}^2 = \text{C} \times \frac{32}{12} = 76.03$$

$$176.99$$

$$\text{O for Fe} = 330.68 \times \frac{16}{56} = 94.48$$

$$\text{O for Zn} = 26.46 \times \frac{16}{65} = 6.51$$

$$\text{O for Mn} = 8.15 \times \frac{16}{55} = 2.37$$

$$\text{O in slag} = 103.36$$

$$\text{Contributed by charges} = 5.44$$

$$\text{Contributed by blast} = 97.92$$

$$\text{To burn sulphides and carbon at the focus} = 176.99$$

$$\text{Total from blast} = 274.91$$

(2) The furnace receives 1,191 pounds of blast per 1,000 of ore smelted. This represents at 0° C.:

$$\frac{1191 \times 16}{1.293} = 14,738 \text{ cubic feet.}$$

Per 2000 lbs. ore	=	29,475	"	"	
Per 68 tons ore	=	2,004,300	"	"	per day
	=	83,510	"	"	" hour.
	=	1,400	"	"	" minute.
At 50° C.	=	1,477	"	"	"
Blower displacement=		4,500	"	"	"

$$\text{Efficiency of blower} = \frac{1,477}{4,500} = 0.328 = 32.8 \text{ per cent. (2)}$$

[It is high time that practical furnace men should stop giving the mechanical displacement of their blower as the amount of air received by their furnace. They still keep doing that, although the furnace receives only from 85 per cent down to 25 per cent of the given volume. What per cent of the piston displacement the furnace is actually receiving is a highly important datum, but is more often unknown than known to the practical men. It can usually only be found by calculation, as is illustrated in the preceding case. We urge upon practical furnace managers, for their own information and use, to cease being satisfied with *piston displacement*, and to get deeper into the real inwardness of their furnace processes by calculating

the *air actually received* by their furnaces. The two things are enough different to make it always "worth while."]

(3) To calculate the heat generated at the focus we will assume that all the fixed carbon of the coke is there burned to CO_2 , and that the rest of the oxygen blown in produces the reaction characteristic of pure pyritic smelting. We have treated per minute

$$\frac{68 \times 2000}{1440} = 94.4 \text{ lbs. of ore.}$$

and the carbon burned per 1000 of ore is 28.51, generating

$$28.51 \times 8100 = 230,930 \text{ lb. Calories.}$$

this absorbs

$$28.51 \times 8/3 = 76.03 \text{ lbs. of oxygen.}$$

leaving $274.91 - 76.03 = 198.88$ lbs. of oxygen to oxidize sulphides.

Since, now, 2O^2 generates by the pyritic smelting reaction 161,560 calories, we have generated per pound of oxygen thus used:

$$161,560 \div 64 = 2,524 \text{ lb. Calories.}$$

and per 1000 of ore smelted we will have

$$2,524 \times 198.88 = 502,000 \text{ lb. Calories.}$$

total heat generated

$$502,000 + 230,930 = 732,930 \text{ lb. Calories.}$$

Since this is per 1000 of ore smelted, per minute we have

$$732,930 \div 1000 \times 94.4 = 77,640 \text{ lb. Calories.}$$

and per square foot of smelting zone area

$$77,640 \div 21.7 = \mathbf{3,575} \text{ lb. Calories.} \quad (3)$$

This last figure is extremely useful in determining the relative activity of different furnaces, and in most cases will be a reliable index of the rate at which the furnace is capable of being driven.

(4) Taking as the basis of calculation 1,000 pounds of ore smelted, there is generated at the focus 732,930 pound Calories, there is used 1,190 pounds of blast, and there arrives at the focus all of the charges except the flue dust, CO^2 of ore, H^2O of quartz, and approximately one-quarter of the sulphur. We therefore, have arriving at the focus about

28.51 lbs. of fixed carbon.
 526.50 lbs. of sulphides.
 621.20 lbs. of inert slag-forming material.

These, assuming them to reach the focus at $1,000^\circ$, would bring back into it the following amounts of heat:

Carbon	$28.51 \times 380 =$	10,834 lb. Calories.		
Sulphides, melted	$526.50 \times 200 =$	105,300	"	"
Slag-forming material	$621.20 \times 174 =$	108,089	"	"
		<hr/>		
		224,223	"	"
Heat generated at the focus	$=$	732,930	"	"
		<hr/>		
Total heat available at the focus	$=$	957,153	"	"

Letting t be the theoretical temperature at the focus, then we have

Heat in Slag	946	$[300 + (t - 1100) 0.27]$
" " Matte	123	$[200 + (t - 1000) 0.14]$
" " S vapor	76	$[179 + (t - 445) 0.11]$
" " SO^2	35	$[0.36t + 0.0003t^2]$
" " CO^2	53	$[0.37t + 0.00022t^2]$
" " N^2	727	$[0.303t + 0.000027t^2]$

[The 76 pounds of sulphur vaporized at the focus is the total sulphur charged, less the 25 pounds assumed as vaporized above the focus, and less the 100.96 pounds oxidized at the focus; the expression is the total heat in 1 pound of sulphur vapor at t , in pound-Calories. The 70 of SO^2 is the weight of sulphur dioxide formed, in pounds, divided by 2.88; the 53 of CO^2 is the weight of CO^2 formed, in pounds, divided by 1.98; the 727 of N^2 is the weight of N^2 divided by 1.26. To be strictly logical the weights of SO^2 , CO^2 and N^2 should be first multiplied by 16 to get ounces, and the resulting expression in ounce-

calories divided by 16 to get pound-Calories. We have simply dispensed with these two numerical operations.]

The sum of the calorific capacity of the products at t° is:

$$20,098 + 530.5t + 0.0425t^2 = 957,153$$

whence

$$t = 1569^\circ \quad (4)$$

It will be noted that the temperature is much higher than could have been attained by attempting to smelt this mixture without coke. If the coke were omitted from the charge we would be without the 28.51 pounds of fixed carbon and some 5.5 pounds of slag-forming material; the products would be without the CO^2 and the N^2 corresponding to it, and the heat available would be decreased 230,930 pound-Calories from the absence of carbon. If these corrections are made, and it is still assumed that the materials come down into the smelting zone at $1,000^\circ$, the theoretically calculated temperature is

$$t = 1447^\circ$$

While this temperature is theoretically sufficient, yet variations in ore quality and temperature and humidity of the air would make running under these conditions much more precarious than with the coke.

(5) This has already been calculated. We found 230,930 pound-Calories to be due to the formation of CO^2 and 502,000 to the oxidation of sulphides, making of the total

$$\begin{array}{r} 31 \text{ per cent from oxidation of carbon} \\ 69 \text{ per cent from oxidation of sulphides.} \end{array} \quad (5)$$

(6) If coke were dispensed with, the theoretical temperature previously attained, $1,569^\circ$, might be reached if the air used were heated. With cold blast we have, under (4), calculated a theoretical temperature of $1,447^\circ$. Under these conditions the heat available was altogether 725,266 pound-Calories. But to heat the products, whose heat capacity was

$$20,083 + 451.7t + 0.0247t^2$$

to $t = 1,569^\circ$ would require (evaluating) 789,600 pound-Calories, which is 64,334 pound-Calories more than are available. To supply this difference by heating the blast we reckon first

the amount of blast per 1,000 of ore smelted, which will be 862 pounds and its heat capacity:

$$\frac{862}{1.293} (0.303t + 0.000027t^2)$$

making this equal to the heat to be supplied, 64,334 lb. Cal. we have

$$202t + 0.01805t^2 = 64,334$$

whence

$$t = 313^\circ. \quad (6)$$

Problem 106.

At Mount Lyell, Tasmania, R. Sticht analyzed the gases at different depths of the shaft in a pyritic smelting furnace, and found them of nearly uniform composition for 6 feet down, leaving out the sulphur vapor, which condensed in taking the samples. At 6 to 7 feet below the top, close to the focus of the furnace, the mean of 5 analyses gave by volume

H ²	0.00
SO ²	0.00
SO ³	7.90
CO ²	3.56
CO	0.00
O ²	0.88
N ² (difference)	87.66

The CO² comes from coke, which it was stated was used to the extent of 1.5 per cent of the charge. The slag contained 53 per cent FeO, 30 per cent SiO².

Required:

- (1) The percentage of the heat generated in the furnace coming from the oxidation of sulphides and the combustion of carbon.
- (2) The heat developed in the furnace per unit of slag formed.
- (3) The volume of blast per 1,000 kg. of slag formed.

Solution:

- (1) We will assume the reaction of oxidation of sulphides to be



and, in fact, the above analyses are our chief justification for so doing. The air blown in is approximately 20.8 per cent of oxygen by volume, and according to the above equation the oxygen going to form FeO is equal to that going to form SO². We have then for the oxygen used

O ² to form 7.90 SO ²	7.90
O ² to form — FeO.....	7.90
O ² to form 3.56 CO ²	3.56
O ² to form 0.88 O ²	0.88
	<hr/>
Sum	20.24
	<hr/>

$$\text{O}^2 \text{ corresponding to N}^2 87.66 \times \frac{20.8}{79.2} = 23.00$$

There is thus a small deficit of oxygen, but if the sulphide oxidizing were assumed to be FeS the reaction would be



and the oxygen accounted for from the gases would be only

O ² to form 7.90 SO ²	7.90
O ² to form — FeO.....	3.95
O ² to form 3.56 CO ²	3.56
O ² to form 0.88 O ²	0.88
	<hr/>
	16.29

which barely accounts for two-thirds of the oxygen which must have accompanied the nitrogen.

The conclusion must therefore be that the sulphide which is being oxidized is Fe²S, and not FeS, for otherwise the gas analyses would show impossible conditions.

The oxidation of the sulphides gives for each O² thus used 161,560 ÷ 2 = 80,780 Calories, and the oxidation of C to CO² 97,200. From the above analyses we infer that for 3.56 volumes of oxygen used for CO² 15.80 volumes were used in oxidizing sulphides. The relative amounts of heat thus generated are therefore:

By carbon $97,200 \times 3.56 = 346,000 = 21.3$ per cent.

By sulphides $80,780 \times 15.80 = 1,276,300 = 78.7$ " " (1)

(2) The production by oxidation of 2FeO (144 kilograms) is accompanied by the production of SO^2 (64 kilograms) and the evolution of 161,560 Calories. The slag being 53 per cent FeO , the slag formed by the reaction is $144 \div 0.53 = 272$ kg. The 64 kg. of SO^2 would be, in volume, 22.22 cubic meters, and would be accompanied in the gases by

$$22.22 \times \frac{3.56}{7.90} = 10 \text{ m}^3 \text{ of } \text{CO}^2.$$

which contains $10 \times 0.54 = 5.4$ kg. of C.
whose heat of oxidation to CO^2 is

$$5.4 \times 8100 = 43,740 \text{ Cal.}$$

but, heat from sulphides = 161,560 "

total heat available 205,300 "

per kg. of slag $205,300 \div 272 = 755$ Cal. (2)

Per unit weight of charge this heat would be slightly lower.

(3) The oxygen used per 272 kg. of slag is

for SO^2	22.22 m ³
" FeO	22.22 "
" CO^2	10.00 "

Total 54.44 "

per kg. of slag 0.20 "

" 1000 kg. of slag 200. "

Volume of air per 1000 kg. of slag made

$$200 \div 0.208 = 960 \text{ cubic meters} \quad (3)$$

SMELTING OF COPPER ORES.

The smelting down to matte is done either in reverberatory furnaces or in shaft furnaces. The charges are usually composed of roasted ore, roasted matte or speiss, mixed with unroasted sulphides, usually concentrates, and with siliceous rock

or limestone as flux. The important reaction during the smelting down is the formation of Cu_2S by the copper present, the formation of other sulphides, mostly FeS , by the larger part of the sulphur left over, and the slagging of the elements which do not enter the matte. If much lead is present metallic lead will separate out, carrying the bulk of the precious metals, but this phenomenon will be considered under the metallurgy of lead. The important subjects for calculation are: the proportions of roasted and unroasted materials to be used, and the proportions of flux to use to make a satisfactory slag.

Some data of importance for calculations on copper smelting have been determined in the author's laboratory by Prof. Walter S. Landis.

A copper matte containing 47.3 copper, 26.2 iron and 23.6 sulphur, was found to have the following thermo-physical characteristics:

Melting point	1,000° C.
Mean specific heat, $0 - t = S_m = 0.21104 - 0.0000366t$	
Actual specific heat, at $t = S = 0.21104 - 0.0000732t$	
Heat content, solid, at 1,000°	= 174 Cal.
Heat content, liquid, at 1,000°	= 204 Cal.
Latent heat of fusion, at 1,000°	= 30 "
Specific heat, at 1,000°	= 0.138

Heat of formation from Cu_2S and FeS not satisfactorily determined.

A copper blast furnace slag containing 35.5 SiO_2 , 39.7 FeO , 1.0 MnO , 11.4 CaO , 2.7 MgO , 9.2 Al_2O_3 , 0.42 Cu , 0.42 S , was found to have the following characteristics:

Melting point	1,114° C.
Mean specific heat, $0 - t = S_m = 0.20185 + 0.0000302t$	
Actual specific heat, at $t = S = 0.20185 + 0.0000604t$	
Heat content, solid, at 1,114°	= 262 Cal.
Heat content, liquid, at 1,114°	= 302 "
Latent heat of fusion, at 1,114°	= 40 "
Specific heat, at 1,114°	= 0.269 "

Heat of formation from its constituent oxides = 133 Calories per kg. of slag.

In the case of the slag, its melting point and latent heat of fusion are not nearly as sharply defined as those of the matte, since the matte melts sharply, but the slag goes through a pasty or viscous stage. The values given are the best approximations which could be gotten from the experiments. As regards heat of formation, the constituent oxides were carefully weighed, mixed with a known weight of carbon, and ignited in a Berthelot bomb calorimeter. Several experiments gave satisfactory concordant results, so that the heat of combination of the constituents of this slag may be taken as not far from 133 Calories per kilo of slag. By following this scheme it is possible to measure experimentally the heat of formation of any slag whose analysis is known.

I. Reverberatory Smelting.

In the reverberatory furnace the atmosphere is in no case strongly reducing; it may be varied from weakly reducing to strongly oxidizing, and in the smelting operation usually averages about neutral. The consequence of this is that copper oxides or sulphate in the charge are not deoxidized by carbon, as in the shaft furnace, nor is Fe^2O^3 reduced to FeO by carbon, but the oxygen thus contained in the charge largely goes off with sulphur as SO^2 , thus decreasing the amount of sulphur left to form matte, and therefore increasing the percentage of copper in the matte formed. The reactions are mainly:



The slag FeSiO^3 is, however, heavy and viscous; it would contain 45 per cent of silica, but runs better and gives a cleaner separation from matte if some lime is added to it. The replacement of 10 per cent of FeO in this silicate by 10 per cent of CaO lowers its melting point from $1,110^\circ \text{C.}$ to $1,010^\circ$, and therefore makes a slag that is much easier to keep fluid and of greater fluidity at any given furnace temperature.

Problem 107.

Peters (*Modern Copper Smelting*, p. 446) gives the composition of the average mixture smelted in the reverberatory furnaces at Argo, Col., as

	<i>Per Cent.</i>
SiO ²	33.9
Iron.....	10.8
BaSO ⁴	15.5
Al ² O ³	5.6
CaCO ³	8.5
MgCO ³	5.8
ZnO.....	6.1
Copper.....	2.0
Sulphur.....	5.1
Oxygen.....	6.4
	<hr/>
	99.7

The furnace smelts 50 tons of this mixture (charged hot, at 350° C.) in 24 hours, using 13.5 tons of bituminous coal and producing a matte with 40 per cent of copper. Outside dimensions of furnace 20 x 40 x 6 feet. Area of stack, fire-box and hearth 16, 32.5 and 481 square feet, respectively. Temperature of stack gases 1,000° C. Composition of the coal: moisture 1.40 per cent, fixed carbon 54.90, volatile matter 32.90, ash 10.80 per cent; assume 10 per cent more air used than necessary for theoretical combustion. Temperature of slag and matte 1,200°.

Required:

(1) The weight of matte produced, assuming the slag to carry 0.2 per cent of copper (as intermingled matte), and the matte 40 per cent.

(2) The loss of copper in the slag, expressed in per cent of the total copper present.

(3) The percentage of the calorific power of the fuel existing in the stack gases, the slag and the matte.

(4) The heat lost by radiation and conduction in pound-Calories per minute per square foot of furnace surface.

(5) The velocity of the hot gases at the base of the stack.

(6) The horse-power theoretically obtainable by passing the hot gases through a boiler which reduces their temperature to 200° C., and which, together with the steam engine, gives a total thermomechanical efficiency of 7.5 per cent upon the heat furnished to (entering) the boiler.

Solution:

(1) The entire matte formed, that free plus that intermingled with the slag, will be per 100 of ore mixture

$$2.0 \div 0.40 = 5.0 \text{ pounds.}$$

	<i>Pounds.</i>
FeS in this matte = $5.0 - 2.5$	= 2.5
Fe in this matte = $2.5 \times 56/88$	= 1.6
Fe going to slag as FeO = $10.8 - 1.6$	= 9.2
FeO in slag = $9.2 \times 72/56$	= 11.8

Constituents of slag:

SiO ₂	= 33.9
FeO	= 11.8
BaO = $15.5 \times 153/233$	= 10.2
Al ₂ O ₃	= 5.6
CaO = $8.5 \times 56/100$	= 4.8
MgO = $5.8 \times 40/84$	= 2.8
ZnO	= 6.1
Weight of slag	= 75.2
Copper in slag as intermingled matte	= 0.15
Intermingled matte lost in slag	= 0.37
Free matte obtained = $5.0 - 0.37$	= 4.63 (1)

$$(2) \quad \frac{0.15}{2.00} = 0.075 = 7.5 \text{ per cent.} \quad (2)$$

(3) The calorific power of the fuel may be calculated from its proximate analysis by the method of Goutal (*Electrochemical and Metallurgical Industry*, April, 1907, p. 145), as follows:

Pure fuel $1.0000 - 0.1220$	= 0.8780
Per cent of this volatile $\frac{0.3290}{0.8780}$	= 37.5 per cent
Calorific power of volatile matter	= 8,650 Cal.
Calorific power (to liquid H ₂ O):	
Carbon $0.5490 \times 8,100$	= 4,447 "
Vol. matter $0.3290 \times 8,650$	= 2,846 "
Sum	= 7,293 "

Water formed = 0.45

Latent heat of vaporization of water

$$= 0.45 \times 606.5 = 273 \text{ Cal.}$$

$$\text{Metallurgical calorific power} = 7,020 \text{ "}$$

Assuming the volatile matter to be 15 per cent hydrogen, 40 per cent oxygen and 45 per cent carbon, the coal contains:

$$\text{Hydrogen} \quad 0.329 \times 0.15 = 0.049$$

$$\text{Volatile carbon} \quad 0.329 \times 0.45 = 0.148$$

$$\text{Fixed carbon} = 0.549$$

$$\text{Total carbon} = 0.697$$

and the air necessary for combustion and products therefrom are per unit weight of fuel used:

$$\text{Oxygen for C} = 0.697 \times 8/3 = 1.859 \text{ pounds.}$$

$$\text{Oxygen for H} = 0.049 \times 8 = 0.392 \text{ "}$$

$$\text{Sum} = 2.251 \text{ "}$$

$$\text{Oxygen in coal} = 0.329 \times 0.40 = 0.132 \text{ "}$$

$$\text{Oxygen needed from air} = 2.119 \text{ "}$$

$$\text{Air needed} = \frac{2.119 \times 13/3 \times 16}{1.293} = 113.7 \text{ cu. ft.}$$

$$\text{Nitrogen therein} = 113.7 \times 0.792 = 90.0 \text{ "}$$

$$10 \text{ per cent surplus air} = 11.4 \text{ "}$$

$$\text{Volume of CO}^2 = \frac{2.556 \times 16}{1.98} = 20.7 \text{ "}$$

$$\text{Volume of H}^2\text{O} = \frac{0.455 \times 16}{0.81} = 9.0 \text{ "}$$

Assuming the tons mentioned are of 2,000 pounds each, the heat generated per 27,000 pounds of fuel used per day is

$$27,000 \times 7,020 = 189,540,000 \text{ pound-Calories,}$$

and, therefore, per 100 pounds of ore smelted:

$$189,540,000 \div 1,000 = 189,540 \text{ pound-Calories.}$$

The fuel used per 100 pounds of ore being 54 pounds, the products of combustion are 54 times the above calculated volumes, to which must be added

$$7.4 \text{ pounds SO}^2 = (7.4 \times 16) \div 2.88 = 41 \text{ cubic feet.}$$

$$6.0 \text{ pounds SO}^3 = (6.0 \times 16) \div 3.60 = 27 \quad " \quad "$$

$$6.7 \text{ pounds SO}^3 = (6.7 \times 16) \div 1.98 = 54 \quad " \quad "$$

found later to be driven off the charge. The stack gases and the heat carried out by them are as follows:

$$\text{CO}^2 \quad 613 \times 0.59 \times 1,000 = 361,670 \text{ ounce-cal.}$$

$$\text{H}^2\text{O} \quad 243 \times 0.49 \times 1,000 = 119,070 \quad " \quad "$$

$$\left. \begin{array}{l} \text{N}^2 \\ \text{Air} \end{array} \right\} 2,738 \times 0.33 \times 1,000 = 903,540 \quad " \quad "$$

$$\text{SO}^2 \quad 41 \times 0.66 \times 1,000 = 27,060 \quad " \quad "$$

$$\text{SO}^3 \quad 27 \times 0.58 \times 1,000 = 15,660 \quad " \quad "$$

$$1,427,000 \quad " \quad "$$

$$= 89,200 \text{ pound-Cal.}$$

Proportion of the calorific power of the fuel in the hot gases:

$$\frac{89,200}{189,540} = 0.47 = 47 \text{ per cent.} \quad (3)$$

To find the heat in the slag tapped, taking Landis's determination of 302 Calories in slag melted at its melting point, $1,114^\circ$, and assuming a specific heat in the melted state of 0.27, we have the heat in it per unit weight at $1,200^\circ$:

$$302 + (0.27 \times 86) = 325 \text{ Cal.}$$

Heat in total slag:

$$325 \times 75.2 = 24,440 \text{ Cal.}$$

Proportion of calorific power of fuel in hot slag:

$$\frac{24,440}{189,540} = 0.129 = 12.9 \text{ per cent.} \quad (3)$$

To find the heat in the matte, we may take Landis's determination of 204 Calories in matte just melted at $1,000^\circ$, and assuming a specific heat of 0.14 we have heat in unit weight at $1,200^\circ$:

$$204 + (0.14 \times 200) = 232 \text{ Cal.,}$$

and, therefore, heat in the matte formed:

$$4.65 \times 232 = 1,080 \text{ Cal.}$$

Proportion of calorific power of fuel in melted matte:

$$\frac{1,080}{189,540} = 0.006 = 0.6 \text{ per cent.} \quad (3)$$

(4) The heat lost by radiation and conduction equals all the heat brought in and generated by combustion and other chemical reactions in the furnace, minus that absorbed by chemical reactions in the furnace, and minus that issuing as sensible heat in the stack gases, slag and matte. The ore mixture being charged hot, at 350° C., and having an assumed specific heat of 0.15, its sensible heat is

	<i>Calories.</i>
$100 \times 0.15 \times 350$	= 5,250
Add heat of combustion of coal	= 189,540

Heat available = 194,790

The heats of chemical reaction of sulphates and oxides on sulphides are quite complex, and we will show the calculation in detail at the end of the problem. Suffice here to give the end results of the calculation:

	<i>Calories.</i>
Chemical reactions, net <i>absorption</i>	16,480
Heat of formation of slag, <i>evolved</i>	+ 9,430
Net heat <i>absorbed</i> in reactions and combinations	7,050
The heat balance sheet will therefore show:	

Available.

	<i>Calories.</i>
Heat in hot charges.....	5,250
Heat of combustion of coal.....	189,540
	<hr/> 194,790

Distribution.

In chimney gases.....	89,200
In liquid slag, tapped out.....	24,440
In liquid matte, tapped out.....	1,080
Absorbed in reactions and combinations.....	7,050
Loss by radiation and conduction.....	77,020
	<hr/> 194,790

The loss by radiation and conduction per day will be:

		<i>Calories.</i>
	$77,020 \times 270$	$= 20,795,000$
per minute	$20,795,000 \div 1,440$	$= 14,400$

The whole outside area of the furnace, including the base, is
 $2 (20 \times 40) + 2 (6 \times 40) + 2 (6 \times 20) = 2,320$ sq. ft.

Loss in pound-Calories per square foot of surface per minute:

$$14,400 \div 2,320 = \mathbf{6.2} \text{ pound-Cal.} \quad (4)$$

(5) The volume of stack gases, at 0°C. , has been found to be 3,662 cubic feet per 100 pounds of fuel used, or $3,662 \times 270 = 988,740$ cubic feet per day = 11.4 cubic feet per second. At $1,000^\circ$ this volume would be

$$11.4 \times (1,000 + 273) \div 273 = 53.2 \text{ cubic feet.}$$

And since the area of stack cross-section is 16 square feet the velocity of the hot gases entering the stack is

$$53.2 \div 16 = \mathbf{3.3} \text{ feet per second.} \quad (5)$$

This is a low velocity and shows good design, which will result in better economy of fuel than if high velocity were used.

(6) The gases were found to contain 89,200 pound-Cal. per 100 of ore smelted, or per day:

$$\begin{array}{rcl} 89,200 \times 1,000 & = & 89,200,000 \text{ pound-Cal.} \\ \text{per hour} & = & 3,717,000 \quad " \quad " \end{array}$$

Since 1 hp. equals 1,400 pound-Cal. per hour, we have:

Horse-power at 100 per cent efficiency:

$$3,717,000 \div 1,400 = 2,650$$

Horse-power at 7.5 per cent efficiency:

$$2,650 \times 0.075 = \mathbf{199} \text{ hp.} \quad (6)$$

In connection with requirement (3) of above problem it will be interesting and instructive to discuss the chemical and especially the thermochemical phenomena accompanying the smelting down of the ore mixture. The discussion will be clearest if we take the actual figures of the problem in question.

Aside from the SiO_2 , Al_2O_3 , etc., the ore mixture contains:

	<i>Per Cent.</i>
Fe.....	10.8
Cu.....	2.0
S.....	5.1
O.....	6.4

and these four ingredients are present either as FeS, FeO, Fe₂O₃, FeSO₄, Cu₂S, Cu₂O, CuO or CuSO₄. With the above quantities of the four elements in question, however, the manner in which they are combined is fixed within rather narrow limits. Each of the four binds each of the others, and it can be found, by some patience and trying out, that the four elements, constituting 24.3 per cent of the ore mixture, must be combined about as follows in order to be present in the quantities given:

	<i>Per Cent</i>
CuO.....	1.0
CuSO ₄	3.0
FeS.....	7.3
FeSO ₄	8.9
FeO.....	0.4
Fe ₂ O ₃	3.7

The best proof of this statement is to resolve the weights of these compounds into their components, and to thus prove that they agree with the premises.

On melting this down to 40 per cent matte we produce

Cu ₂ S.....	2.5 per cent in matte,
FeS.....	2.5 per cent in matte,
SO ₂	7.4 per cent in gases,
FeO.....	11.8 per cent to slag.

The heat represented by the formation of the products must be subtracted from the heat of formation of the materials reacting to get the net heat of the reaction. We will multiply the amount of each material by the heat of formation of unit weight from its elements as follows:

		<i>Cal.</i>
CuO	$1.0 \times (37,700 \div 79.6) = 1.0 \times 473$	= 473
CuSO ₄	$3.0 \times (181,700 \div 159.6) = 3.0 \times 1,139$	= 3,417
FeS	$7.3 \times (24,000 \div 88) = 7.3 \times 273$	= 1,993

FeSO ⁴	$8.9 \times (214,500 \div 152) = 8.9 \times 1,411$	= 12,558
FeO	$0.4 \times (65,700 \div 72) = 0.4 \times 913$	= 365
Fe ² O ³	$3.7 \times (195,600 \div 160) = 3.7 \times 1,223$	= 4,525

Sum = 23,331

Heat of formation of products:

Cu ² S	$2.5 \times (20,300 \div 159) = 2.5 \times 128$	= 320
FeS	$2.5 \times (24,000 \div 88) = 2.5 \times 273$	= 683
SO ²	$7.4 \times (69,260 \div 64) = 7.4 \times 1,082$	= 8,007
FeO	$11.8 \times (65,700 \div 72) = 11.8 \times 913$	= 10,773

Sum = 19,782

Difference, heat absorbed = 3,549

We have, therefore, a deficit, or heat to be supplied. This deficit is increased by the heat required to decompose BaSO⁴ into BaO and SO³, CaCO³ into CaO and CO² and MgCO³ into MgO and CO²; while it is decreased by the heat of combination of Cu²S and FeS to form matte, and the heat of combination of SiO² with BaO, Al²O³, CaO, MgO, ZnO and FeO to form slag.

The driving off of SO³ and CO² absorbs

	<i>Calories.</i>
SO ³ from BaO, SO ³	$6.0 \times 1,189 = 7,134$
CO ² from CaO, CO ²	$3.7 \times 1,026 = 3,796$
CO ² from MgO, CO ²	$3.0 \times 666 = 1,998$

Sum = 12,928

The net result of all these reactions, leaving out the formation heat of the slag from its oxide constituents, is

	<i>Lb. Cal.</i>
Absorbed	$23,331 + 12,928 = 36,259$
Evolved	19,782
Deficit	<hr/> 16,477

And even if we credit the heat of formation of the slag:

	<i>Lb. Cal.</i>
70.9×133	= 9,430
there remains a net deficit of	<hr/> 7,047

The reaction of the ore mixture to form matte and slag is therefore an endothermic operation, in spite of the fact that much sulphur goes off as SO^2 . The prime reason for this is that the bulk of the sulphur in the roasted ore was present as sulphate and not as sulphide.

Problem 108.

A copper blast furnace has at its disposal materials of the following compositions in percentages:

	<i>Cu.</i>	<i>Fe.</i>	<i>S.</i>	<i>SiO</i> ² .
Selected raw ore.....	15	20	35	25
Roasted concentrates....	25	35	10	12
Refinery slag.....	50	10	—	25
<hr/>				
Limestone.....	CaO — 50			1

It is desired to make a matte with 50 per cent copper and a slag containing 35 per cent SiO^2 , 40 per cent FeO and 15 per cent CaO , or with these ingredients in those proportions.

Required:

- (1) The proportions of charge.
- (2) A balance sheet showing distribution of these materials.

Solution: The foregoing conditions are those which frequently confront the copper smelter. He has at hand raw ore and roasted concentrates, whose relative quantities he can usually vary at will by simply concentrating and roasting more or less material. He has return slags from the refinery furnaces which, however, are not unlimited in quantity, but bear a general relation to the weight of matte made and sent on to the further operations. Finally, the limestone can be varied at will. It will readily be seen that if the charge is fixed at a certain quantity of raw ore to start with, that there are then three variables, the quantities of the other three materials, and to fix these there are practically only two conditions to be fulfilled, the two ratios between three components of the slag. In order to make a solution possible, it is necessary to make an assumption which will practically reduce the number of variables by one, and on looking over the ground it is seen that the most rational assumption which can be made is to assume the refinery slag to bear a given relation to the weight of matte produced. Such an assumption eliminates the weight

of refinery slag as a variable, and leaves us with only two variables and two conditions to fill, which makes a solution possible. Assuming the charges to be based on 100 of roasted ore, we can call the weight of roasted concentrates used X , the weight of refinery slag Y , and the weight of limestone Z , and then figure out the weight of matte produced in terms of X , Y and Z . Assuming then that the refinery slag is, say, 0.25 of the weight of matte, we have $Y = \frac{1}{4}$ (expression for weight of matte), and thus one equation between X , Y and Z . The ingredients of the slag being figured out in terms of X , Y and Z , the assumed relations between FeO , CaO and SiO_2 in the slag give us two more equations between X , Y and Z , and thus all three quantities can be determined.

The provisional balance sheet, based on 100 of ore and X , Y and Z of other ingredients of the charge, will be as follows:

BALANCE SHEET.

Ore. (100).	Matte.	Slag.
Cu 15	Cu 15	
Fe 20	Fe $7.2 + 0.14Y$	FeO $16.5 - 0.18Y$
S 35	S $7.8 + 0.03X + 0.26Y$	
SiO_2 25		SiO_2 25.0
<i>R'st'd</i>		
<i>Conc. (X).</i>		
Cu 0.25X	Cu 0.25X	
Fe 0.35X	Fe 0.12X	FeO 0.30X
S 0.10X	S 0.10X	
SiO_2 0.12X		SiO_2 0.12X
<i>Ref.</i>		
<i>Slag. (Y).</i>		
Cu 0.50Y	Cu 0.50Y	
Fe 0.10Y	Fe 0.10Y	
SiO_2 0.25Y		SiO_2 0.25Y
<i>Lime-</i>		
<i>stone. (Z).</i>		
CaO 0.50Z		CaO 0.50Z
SiO_2 0.01Z		SiO_2 0.01Z

Notes on above balance sheet:

Copper in the matte.....	15	$+ 0.25X + 0.50Y$
Weight of matte (50 per cent Cu).....	30	$+ 0.50X + 1.00Y$

Weight of S in matte..... $7.8 + 0.13X + 0.26Y$

Weight of Fe in matte..... $7.2 + 0.12X + 0.24Y$

These weights of S and Fe are therefore provided for under the column "matte," taking them from the various materials charged.

The refinery slag being assumed 0.25 of the matte, we have at once

$$\begin{aligned} Y &= 0.25 (30 + 0.50X + 1.00Y) \\ &= 7.5 + 0.13X + 0.25Y \end{aligned}$$

whence $Y = 10 + 0.17X$

That is, the refinery slag equals in weight 0.1 the ore plus 0.17 the roasted concentrates. This practically amounts to leaving the roasted concentrates and limestone as the only variables.

The problem can now be solved by summing up the ingredients of the slag as follows:

$$\begin{aligned} \text{FeO} &= 16.5 - 0.18Y + 0.30X \\ \text{SiO}_2 &= 25.0 + 0.25Y + 0.12X + 0.01Z \\ \text{CaO} &= 0.5Z \end{aligned}$$

$$\begin{aligned} \text{or substituting } Y &= 10 + 0.17X \\ \text{FeO} &= 14.7 + 0.27X \\ \text{SiO}_2 &= 27.5 + 0.16X + 0.01Z \\ \text{CaO} &= 0.5Z \end{aligned}$$

And since the requirements of the slag are that

$$\text{SiO}_2 = \frac{35}{40} \text{FeO}$$

and

$$\text{CaO} = \frac{15}{40} \text{FeO}$$

we have:

$$27.5 + 0.16X + 0.01Z = \frac{35}{40} (14.7 + 0.27X)$$

$$0.50Z = \frac{15}{40} (14.7 + 0.27X)$$

whence

$$X = 195 \quad Z = 48$$

and, therefore,

$$Y = 43$$

The final balance sheet then becomes

BALANCE SHEET.			
<i>Ore.</i>	(100).	<i>Matte.</i>	<i>Slag.</i>
Cu	15	Cu 15	
Fe	20	Fe 20	
S	35	S 35	
SiO ²	25		SiO ² 25
<i>Rs't'd Conc.</i>	(195).		
Cu	49	Cu 49	
Fe	68	Fe 17	FeO 66
S	20	S 10	
SiO ²	23		SiO ² 23
<i>Ref. Slag.</i>	(43).		
Cu	22	Cu 22	
Fe	4	Fe 4	
SiO ²	11		SiO ² 11
<i>Limestone.</i>	(48).		
CaO	24		CaO 24
SiO ²	1		SiO ² 1
		<hr/>	<hr/>
		172	150
<i>Matte.</i>	<i>Per Cent.</i>	<i>Slag.</i>	<i>Ratio.</i>
Cu.....	86 = 50	SiO ²	60 = 36
Fe.....	41 = 24	FeO.....	66 = 40
S.....	45 = 26	CaO.....	24 = 14
	<hr/>		<hr/>
	172		150 90

Furnace managers are usually afraid of X, Y and Z, and in regular running there is usually little need for an algebraic solution, yet many occasions arise when a judicious use of algebra solves a problem in an exact manner which hardly any amount of guessing or approximating can attain efficiently. In bringing forward this solution we may lay ourselves open to being called pedantic or academic, but the fact is that *the conditions of this problem* were proposed to the writer as a difficult nut to crack by a practical copper smelter, and the algebraic solution furnished was characterized by him as the most satisfactory solution of this class of problems which he had yet seen.

"Bringing Forward" of Copper Matte.

The above term is the old Welsh expression for the further treatment of mattes which gradually eliminates iron and sulphur and finally results in "crude" or "blister" copper, usually 90 to 99 per cent pure. The matte obtained by the first smelting operation varies considerably in richness, between 20 and 50, or even up to 60 per cent, of copper. The reason it is not always made high in copper is that the richer the matte the more copper goes into the slag; one of the expert metallurgist's best accomplishments in copper smelting is to make a rich matte and poor slag. The making of slag of the best composition, and the use of extra large settlers or fore-hearths, helps most to this end. Having then this first "matte" the problem of the metallurgist is to get from it the metallic copper which it contains.

THE WELSH PROCESS.

The principle employed is to partially roast the matte and then to smelt it down to a richer matte and a ferruginous slag. The grade of matte formed in this smelting depends entirely upon the amount of roasting to which the matte has been subjected, the more sulphur eliminated by roasting the less can be present to form matte and the richer the matte.

Illustration: A matte containing 21.36 per cent of copper and 22.95 per cent of sulphur is roasted until its sulphur contents is two-thirds eliminated. What grade of matte can be expected on the subsequent smelting.

The sulphur left is $22.95 \div 3 = 7.65$. The 21.36 of copper requires 5.34 of sulphur to form Cu_2S , leaving $7.65 - 5.34 = 2.31$ of sulphur to form FeS . This forms $2.31 \times 88/32 = 6.35$ FeS . The resulting matte cannot contain more FeS than this; its composition will therefore be approximately:

Copper.....	21.36 = 64 per cent
Iron.....	4.04 = 12 "
Sulphur.....	7.65 = 23 "
	<hr/>
	33.05

In practical work a richer matte than this will be formed in reverberatory furnace smelting and a slightly poorer matte by shaft furnace smelting, because in the former there is some

reaction between the oxides and sulphides of the roasted ore, resulting in an expulsion of SO_2 during smelting, and in the latter, using carbonaceous fuel, the temperature is so high and reducing action so strong that metallic iron is formed and enters the matte, practically acting as if the matte contained some Fe_2S , and thus diluting the matte.

This roasting is a slow operation unless the matte is crushed and roasted fine. Lump matte is very little pervious to gases; it roasts slowly. By breaking a lump in half we, on an average, increase its surface 50 per cent, and therefore the exposed surface available for oxidation increases, for a given weight of material, very quickly as its size is decreased. For auto-roasting by its own self-generated heat of oxidation the finer the better, and roasting thus in lump form is impracticable because of the slowness of the operation.

Pyritic smelting of matte is probably altogether out of question as far as pure pyritic smelting without carbonaceous fuel is concerned. Using some coke, however, an oxidizing smelting analogous to partial pyritic smelting is possible, as was proved by Mr. Freeland, at Isabella, Tenn. Such a concentrating pyritic smelting is more feasible with a low-grade matte than with a high grade, because there is more iron and sulphur to oxidize. It will be profitable to calculate closely the details of this matte smelting to rich matte, and to compare it with the details of the smelting of raw ore in the same furnace—the subject of Problem 105, page 463.

Problem 109.

W. H. Freeland at Isabella, Tenn. (see *Engineering and Mining Journal*, May 2, 1903), smelted a low-grade matte without preliminary roasting in a water-jacketed Herreshoff furnace, having a free area at the tuyeres of 21.7 square feet. The analyses of materials used and the products are as follows:

Charges.

	Matte.	Raw Laboratory				
		Ore.	Samplings.	Slags.	Quartz.	Coke.
Cu.....	20.00	2.79	2.45	0.73
Fe.....	47.15	43.26	31.07	39.20	1.45	2.30
S.....	24.00	29.18	14.84	1.75	0.32	1.58
SiO_2	0.44	10.01	22.66	30.90	96.79	8.41

	<i>Matte.</i>	<i>Ore.</i>	<i>Samplings.</i>	<i>Slags.</i>	<i>Quartz.</i>	<i>Coke.</i>
CaO.....	0.10	6.32	5.71	8.51	0.23
MgO.....	1.39	2.03	2.71
Zn.....	2.05	2.56	2.05	2.88	0.00
Al ² O ³	0.82	1.00	1.15	1.90	0.32	3.56
Mn.....	0.53	0.69	0.75	0.85	0.00
O.....	4.91	3.39	11.37	0.38	1.00
C.....	13.90	83.86
CO ² , etc.....	2.80
Loss.....	0.39

Products.

	<i>Matte.</i>	<i>Flue Dust.</i>	<i>Slag.</i>
Cu.....	49.63	2.49	0.60
Fe.....	25.24	24.79	43.99
S.....	23.00	8.91	1.19
SiO ²	0.26	31.43	33.72
CaO.....	3.31	2.03
MgO.....	1.18	0.57
Zn.....	1.53	3.81	2.12
Al ² O ³	3.93	2.16
Mn.....	0.39	0.30	0.50
O.....	3.97	12.86
C.....	15.88

The charges and products per 24 hours and per 1,000 of matte used were:

Charges.

Matte.....	47.5 tons	1,000 lbs.
Raw Ore.....	8.1 "	170 "
Laboratory samplings	1.6 "	34 "
Slag.....	7.6 "	160 "
Quartz.....	15.7 "	330 "
Coke.....	4.5 "	95 "

Products:

Matte.....	19.1 tons	401.6 lbs.
Flue dust.....	0.6 "	12.0 "
Slag.....	56.1 "	1182.2 "

Blast applied, 4,500 cubic feet displacement, at 17 ounces pressure. Assume temperature of gases 450° C., and that they

contain no CO , SO^3 or free O^2 (no analyses are given). Assume matte and slag issuing from the furnace at $1,300^\circ \text{C}$. (no temperature is given).

Required:

(1) A balance sheet of everything entering and leaving the furnace.

(2) The volume efficiency of the blowing plant.

(3) The heat generated per minute per square foot of cross-section in the focus of the furnace.

(4) The theoretical temperature at the focus.

(5) The proportion of the heat generated in the focus by the combustion of carbon and by the oxidation of sulphides.

(6) The concentration effected in this smelting.

(1) **Balance Sheet** (per 1000 of *matte smelted*).

<i>Charges.</i>		<i>Matte.</i>	<i>Flue Dust.</i>	<i>Slag.</i>	<i>Gases.</i>
Matte (1,000)					
Cu	200.00	199.31	0.30	0.39
Fe	471.50	101.36	2.97	367.17
S	240.00	92.18	147.82
SiO^2	4.40	1.04	3.36
CaO	1.00	1.00
Zn	20.50	6.14	14.36
Al^2O^3	8.20	8.20
Mn	5.30	1.57	3.73
O	49.10	49.10

Ore (170)

Cu	4.74	4.74
Fe	73.54	73.54
S	49.60	1.07	14.15	34.38
SiO^2	17.02	3.77	13.25
CaO	10.74	0.40	10.34
MgO	2.36	0.14	2.22
Zn	4.35	0.46	3.89
Al^2O^3	1.70	0.47	1.23
Mn	1.17	0.04	1.13
O	2.40	2.40
CO^2	2.38	2.38

<i>Charges.</i>		<i>Matte.</i>	<i>Flue Dust.</i>	<i>Slag.</i>	<i>Gases.</i>
Samplings (34)					
Cu	0.83	0.83
Fe	10.56	10.56
S	5.05	5.05
SiO ²	7.70	7.70
CaO	1.94	1.94
MgO	0.69	0.69
Zn	0.70	0.70
Al ₂ O ₃	0.39	0.39
Mn	0.26	0.26
O	1.15	0.48	0.67
C	4.73	1.91	2.82
Slags (160)					
Cu	1.17	1.17
Fe	62.72	62.72
S	2.80	2.80
SiO ²	49.44	49.44
CaO	13.62	13.62
MgO	4.34	4.34
Zn	4.61	4.61
Al ₂ O ₃	3.04	3.04
Mn	1.36	1.36
O	16.90	16.90
Quartz (330)					
Fe	4.78	4.78
S	1.06	1.06
SiO ²	319.41	319.41
CaO	0.76	0.76
Al ₂ O ₃	1.06	1.06
H ₂ O	2.93	2.93
Coke (95)					
Fe	2.19	2.19
S	1.50	1.50
SiO ²	7.99	7.99
Al ₂ O ₃	3.38	3.38
C	79.67	79.67
H ₂ O	0.27	0.27

<i>Charges.</i>		<i>Matte.</i>	<i>Flue Dust.</i>	<i>Slag.</i>	<i>Gases.</i>
Blast (2,065)					
O ²	476.63	81.24	395.39
N ²	1588.77	1588.77
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
(3854)		401.60	12.01	1176.05	2264.84

Notes on the Balance Sheet.

The sulphur and carbon of the charge passing into the gases are, from the balance sheet, 192.61 and 82.49, respectively. We can assume all the carbon in the gases as CO² and all the sulphur as SO² except, say, half of that from the ore. This leaves 192.61 - 17.19 = 175.42 of sulphur to be oxidized at the focus:

$$\text{Oxygen for sulphur} = 175.42 \times \frac{32}{32} = 175.42$$

$$\text{Oxygen for carbon} = 82.49 \times \frac{38}{16} = 219.97$$

$$\text{Total to burn sulphur and carbon at focus} = \underline{395.39}$$

$$\text{Oxygen for Fe in slag} = 499.31 \times \frac{16}{56} = 142.66$$

$$\text{Oxygen for Mn in slag} = 6.48 \times \frac{16}{55} = 1.88$$

$$\text{Oxygen for Zn in slag} = 23.56 \times \frac{16}{65} = 5.77$$

$$\text{Total in slag} = \underline{150.31}$$

$$\text{Total oxygen in gas and slag} = 545.70$$

$$\text{Oxygen furnished by solid charges} = \underline{69.07}$$

$$\text{Oxygen furnished by the blast} = 476.63$$

$$\text{Nitrogen furnished by the blast} = 1588.77$$

(2) The furnace receives 2,065 pounds of blast per 1,000 of matte concentrated. This represents at 0°:

$$\frac{2065 \times 16}{1.293} = 25,550 \text{ cubic feet.}$$

Per 2000 lbs. matte	=	51,100	"	"	
Per 47.5 tons matte	=	2,427,250	"	"	per day.
	=	101,135	"	"	" hour.
	=	1,686	"	"	" minute.
At 50° C.	=	1,958	"	"	" "
Blower displacement	=	4,500	"	"	" "

$$\text{Efficiency of blower} = \frac{1,958}{4,500} = 0.435 = 43.5 \text{ per cent.} \quad (2)$$

(3) To calculate the heat generated at the focus we will assume that all the fixed carbon of the coke is there burned to CO^2 , and that the rest of the oxygen blown in produces the reaction characteristic of pure pyritic smelting. There is treated per minute:

$$\frac{47.5 \times 2000}{1440} = 66 \text{ lbs. of matte,}$$

and the carbon burned per 1000 of matte is 82.49 lbs., generating

$$82.49 \times 8100 = 668,169 \text{ lb.-Calories,}$$

and absorbing 219.97 lbs. of oxygen. This leaves $476.63 - 219.97 = 256.67$ lbs. of oxygen to oxidize sulphides.

Since by the "pyritic smelting" reaction, 2O^2 generates 161,560 calories, there is generated per pound of oxygen thus used

$$161,560 \div 64 = 2,524 \text{ lb.-Calories,}$$

and per 1000 lbs. of matte smelted we have

$$2,524 \times 256.67 = 677,820 \text{ lb.-Calories,}$$

$$\begin{array}{rcl} \text{but heat generated by carbon} & = & 668,170 \text{ " " } \\ \text{Total} & = & 1,345,990 \text{ " " } \end{array}$$

Since this is per 1000 lbs. of matte smelted, we have, per minute

$$1,345,990 \div 1,000 \times 66 = 88,835 \text{ lb.-Calories,}$$

and per square foot of smelting zone area, per minute

$$88,835 \div 21.7 = 4,094 \text{ lb.-Calories.} \quad (3)$$

Comparing this with the 732,930 pound-Cal. generated at the focus in smelting 1,000 pounds of ore and the 3,575 pound-Cal.

there generated per square foot per minute, we see that the matte smelting requires more heat per unit of charge, principally because the smelting is done more slowly. Radiation losses are over twice as great per unit of charge treated when concentrating matte than when ore concentrating. This points to the utility of hard driving when smelting matte, as the direction likely to yield greatest economy.

(4) Taking as a basis of calculation 1,000 pounds of matte treated, there is generated at the focus 1,345,900 pound-Cal., there is used 2,065 pounds of blast, and there arrives at the focus all of the charges except the flue dust, CO_2 and H_2O of charges, and approximately one-half of the sulphur contained in the raw ore. We therefore have arriving at the focus approximately:

82.5 lbs. of fixed carbon,
1133.0 lbs. of sulphides.
545.0 lbs. of inert slag-forming material.

These come to the focus preheated by the ascending gases, and assuming them to be preheated to $1,000^\circ$, we can find the correction to be used for their sensible heat:

Carbon	$82.5 \times 380 =$	31,350 lb. Calories.
Sulphides, melted	$1133.0 \times 200 =$	226,000 " "
Slag-forming material	$545.0 \times 174 =$	94,850 " "
		<hr/>
		352,200 " "
Heat generated at the Focus		<hr/>
		1,345,990 " "
		<hr/>
Total in the hot products, at Focus		1,698,190 " "

Letting t be the theoretical temperature at the focus, then we have:

Heat in Slag	1176	$[300 + (t - 1100)0.27]$
" " Matte	402	$[200 + (t - 1000)0.14]$
" " S vapor	17	$[179 + (t - 445)0.11]$
" " SO_2	$\frac{351}{2.88}$	$[0.36t + 0.0003t^2]$
" " CO_2	$\frac{302}{1.96}$	$[0.37t + 0.00022t^2]$
" " N_2	$\frac{1589}{1.26}$	$[0.303t + 0.000027t^2]$

The calorific capacity of these products at t° is therefore

$$29,858 + 858.7t + 0.1046t^2$$

and making this equal to the heat available at the focus, we have

$$0.1046t^2 + 858.7t + 29,858 = 1,698,190$$

whence

$$t = 1622^\circ. \quad (4)$$

This is 53° higher than we calculated for the same furnace smelting ore, with only one-third as much coke. If the coke were omitted from this charge the theoretical temperature would be:

$$t = 1388^\circ.$$

Such a theoretical temperature at the focus would not suffice to form slag, supply radiation and conduction losses, and see the matte and slag safely out of the furnace, except with very hard driving and very fast running in a large furnace.

(5) The heat generated by oxidation at the focus has already been calculated. The proportion to credit to carbon is

$$\frac{668,170}{1,345,990} = 0.496 = 49.6 \text{ per cent.}$$

and to oxidation of sulphides **50.4** " (5)

In the ore smelting these figures were found to be 31 and 69 per cents, respectively.

(6) The ratio of concentration is usually found by comparing the per cent of copper in the material treated with that in the material produced. This would give in this case:

$$\frac{49.64}{20.00} = 2.48 \quad (6)$$

A more reasonable factor, however, is the ratio of weight of fresh copper-bearing materials treated to weight of copper-bearing materials produced which must be further treated. This would be in this case:

$$\frac{1204}{414} = 2.9$$

whereas in the ore smelting it was

$$\frac{1080}{148} = 7.3$$

"Blister-Roasting" or "Roasting-Smelting."

When a matte has been concentrated to somewhere between 70 and 80 per cent of copper it is called "white metal," and is in shape for reduction to metallic copper:

	<i>Cu</i> ² <i>S</i> .	<i>FeS</i> .
With 70 per cent copper, matte contains...	87.5	12.5
With 80 per cent copper, matte contains...	100.0	0.0

The problem being to get metallic copper, the operation is entirely one of oxidation; first, slow melting down of the lumps of matte in a highly oxidizing atmosphere on the hearth of a reverberatory furnace; second, continued oxidation until all the sulphur is removed and the bath remains as metallic copper, saturated with *Cu*²*O* and *Cu*²*S*.

During the melting down the matte is oxidized superficially to such an extent that when fusion is finally complete the copper oxides have reacted upon the iron sulphides sufficiently to eliminate all the iron from the matte. The reactions and phenomena of this period are exactly those of the matte concentration processes.

After the melting down sulphur continues to be oxidized with formation of copper oxide, and then this latter reacts with more of the sulphide to set free metallic copper.

- (a) $2\text{Cu}^2\text{S} + 3\text{O}^2 = 2\text{Cu}^2\text{O} + 2\text{SO}^2.$
- (b) $\text{Cu}^2\text{S} + 2\text{Cu}^2\text{O} = 6\text{Cu} + \text{SO}^2.$
- (c) $\text{Cu}^2\text{S} + \text{O}^2 = \text{Cu} + \text{SO}^2.$

Reactions (a) and (b) are probably consecutive, but assuming them simultaneous we have equation (c).

Thermochemically, equation (a) analyzes as follows:

$2(\text{Cu}^2, \text{S})$	$= 2(20,300)$	$= 40,600$	Calories <i>absorbed</i> .
$2(\text{Cu}^2, \text{O})$	$= 2(43,800)$	$= 87,600$	" <i>evolved</i> .
$2(\text{S}, \text{O}^2)$	$= 2(69,260)$	$= 138,520$	" "
Algebraic sum		$= 185,520$	" "
Per kilo. of Cu^2S		$= 580$	" "

Similarly, equation (b):

(Cu^2, S)	$= 20,300$	Calories <i>absorbed</i> .
$2(\text{Cu}^2, \text{O})$	$= 2(43,800)$	$= 87,600$ " "
(S, O^2)	$= 69,260$	" <i>evolved</i> .
Algebraic sum		$= 38,640$ Calories <i>absorbed</i> .
Per kilo. of Cu^2S		$= 243$ " "

Equation (c) gives:

(Cu^2, S)	$= 20,300$	Calories <i>absorbed</i> .
(S, O^2)	$= 69,260$	" <i>evolved</i> .
Algebraic sum		$= 48,960$ " "
Per kilo. of Cu^2S		$= 308$ " "
Per kilo. of copper liberated		$= 385$ " "

The net result of these figures is to show that the first reaction evolves a large amount of heat, that the second absorbs considerable, but that the two together constitute a highly exothermic reaction. When we reflect that a kilogram of melted Cu^2S only carries some 250 Calories, and a kilogram of melted copper not over 200 at any furnace temperature, the excess of heat above calculated shows up very strikingly.

In a reverberatory furnace the rate of oxidation is so slow that but minor advantage is taken of the heat of oxidation of the Cu^2S .

Illustration: In a reverberatory furnace, 8 tons of "white metal" is smelted to blister copper in 48 hours, using 5 tons of coal. About what proportion does the heat of oxidation of the charge bear to the heat of combustion of the coal?

Assuming the tons to be 1,000 kilos., the white metal to be

nearly pure Cu_2S , and the calorific power of the coal 6,000, we have:

Heat of oxidation of the bath $8000 \times 308 = 2,464,000$ Calories.

" of combustion of coal $5000 \times 6000 = 30,000,000$ "

" requirement for 48 hours $32,464,000$ "

" requirement per hour $676,333$ "

Proportion of heat requirement furnished by oxidation of bath:

$$\frac{2,464,000}{34,920,000} = 0.759 = 7.6 \text{ per cent.}$$

The above figures teach us, however, that when the charge is once melted, if the oxidation of the bath could be performed quickly enough it alone would keep the furnace up to heat. For example, the furnace requires an average of 727,500 Cal. per hour to keep it up to heat. The heat of oxidation would therefore supply this for

$$\frac{2,464,000}{727,500} = 3\frac{1}{2} \text{ hours,}$$

which means that if the bath, when melted, could be oxidized in that time all exterior firing would be unnecessary after the charge had been once melted. Some companies force air onto the surface of the bath, and one company blows compressed air through wrought iron pipes into the bath, producing the required oxidation in one-fifth the time usually required, and saving greatly in coal.

Bessemerizing Copper Matte.

John Hollaway, in 1878, patented the process of oxidizing matte to metallic copper in an apparatus similar to the Bessemer steel converter; in 1880, Manhès, in France, was successful in accomplishing this result, and in 1884 ran the first commercial plant at the Parrot works in Butte. While the principles are similar the details are very different from the blowing of pig iron to steel.

In oxidizing pig iron the carbon silicon, manganese, etc., which are to be oxidized out rarely exceed 10 per cent, while

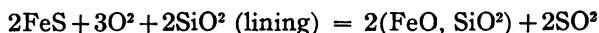
the iron itself is oxidizable, and some 3 to 20 per cent may be lost. In oxidizing matte some 40 to 70 per cent of the whole charge is to be oxidized, a very voluminous slag results; and the operation lasts five to fifteen times as long. Towards the end of a "steel" blow, the pure iron formed is itself oxidizable, and is not chilled but really heated by the passing of the blast through it; in a "matte" blow the pure copper separating at the end is not oxidizable under the prevailing conditions, and therefore is only chilled by the blast if the latter strikes it. On the latter account, tuyeres in the bottom are impracticable when Bessemerizing matte, since they become filled with chilled copper; it is imperative to use lateral tuyeres which, by the swinging of the converter, are kept always below the surface of the matte but above the pool of copper as it separates out and sinks to the bottom.

The two best treatises for details of bessemerizing copper matte are *Jannettaz's "*Les Convertisseurs pour le Cuivre*" and Dr. F. Mayr's "*Das Bessemern von Kupfersteinen*;" very satisfactory information can be found in Dr. Peters' "*Modern Copper Smelting*" and "*Principles of Copper Smelting*," in Hixon's "*Notes on Lead and Copper Smelting and Copper Converting*," and in Schnabel's "*Handbook of Metallurgy*," last edition, Vol. I.

Assume that a converter is just emptied, is at a bright red heat ($1,100^{\circ}$), and that a charge of melted matte at, say, $1,100^{\circ}$ (setting point $1,000^{\circ}$), is poured into it. The lining is some 60 cm. thick, the outside shell of the converter is at about 200° C., and the surface is losing heat at a nearly steady rate of, say, 50 Cal. per square meter of outside surface per minute (10 pound-Cal. per square foot). A converter of 25 square meters outside surface would thus lose 1,250 Cal. per minute if standing still. If it had 3,000 kg. of liquid matte in it, with a specific heat of 0.14, the latter would give out $3,000 \times 0.14 = 420$ Calories for every degree which it cooled, and would therefore cool off about $1,250 \div 420 = 3^{\circ}$ per minute. If poured in 100° above its setting point it might be some 30 minutes in cooling to its setting point and 70 minutes in setting, assuming no radiation losses through the throat, *i.e.*, that the throat were tightly covered.

* Mem. de la Soc. Ing. Civile, 1902, (I), 268-319.

Under such conditions, if blast is turned on, the reaction is



and the heat evolved is

Decomposition of	2FeS	= 2(24,000)	= - 48,000	Calories.
Formation of	2FeO	= 2(65,700)	= + 131,400	"
Union of 2FeO with	2SiO ²	= 2(8,900)	= + 17,800	"
Formation of	2SO ²	= 2(69,260)	= + 138,520	"
Total = + 239,720				"

Heat evolution per 1 kg. FeS = 1,362 Calories.

Heat evolution per 1 kg. O² = 2,497 "

THEORETICAL TEMPERATURE RISE.

Supposing we oxidize an amount of FeS equal to 1 per cent of the weight of matte. Let us calculate the theoretical rise in temperature of the contents of the converter.

The oxygen required is 3O² to 2FeS, or per kilo. of FeS.

Oxygen required = $96 \div 176 = 0.545$ kg.

N² accompanying = 1.818 "

Air required = 2.363 "

Volume = $2.363 \div 1.293 = 1.827$ m³.

In being raised from say 50° C. to 1100°, the assumed temperature of the matte, the air will absorb

$$1.827[0.303 + 0.000027(1150)] \times 1050 = 641 \text{ Calories.}$$

This leaves available, for raising the temperature of the products of the reaction:

$$1,362 - 641 = 721 \text{ Calories.}$$

The immediate products are:

- 99. kg. of unoxidized matte.
- 1.50 " " liquid slag.
- 0.73 " " SO² gas.
- 1.82 " " N² gas.

The heat capacities of these, at 1100°, are as follows, per 1° C.:

Matte	$99 \times 0.14 = 13.86$	Calories.
Slag	$1.50 \times 0.27 = 0.41$	"
SO ²	$0.73 \div 2.88 \times 1.02 = 0.25$	"
N ²	$1.818 \div 1.26 \times 0.36 = 0.52$	"
	Sum = 15.04	"

Theoretical temperature rise

$$721 \div 15.04 = 47.9^\circ \text{ C.}$$

The above rise represents the *rate* at which the temperature tends to rise at the beginning of the blow. Supposing this amount of FeS (1 per cent) is oxidized in 1 minute, the temperature at the end of 1 minute would rise 47.9° less the cooling off in 1 minute, which latter might be from 2° to 10°, according to the size of the converter and its charge, thickness of lining, etc. For practical purposes the cooling-off rate may be assumed as nearly constant, but the heating-up rate is quite variable. As the FeS disappears the amount of slag increases, while that of the matte decreases; but since 1.50 kilos. of slag with a calorific capacity of 0.41 Cal. per degree takes the place of 1 kilo. of matte with a calorific capacity of 0.14 Cal. per 1°, the heat capacity of the products is increasing 0.27 Cal. for each 1 per cent. of FeS oxidized, while the available heat for raising temperature is slightly decreasing, because of the higher temperature of the bath and therefore the greater chilling effect of the air. Assuming that the bath cools 5° during the time that 1 per cent of FeS is being oxidized out, we can calculate the following table:

FeS	Temp.	Heat	Net	Calorific	
Oxidized.	at	Absorbed	Heat	Capacity	Temp.
	Start.	by Air.	Available.	of	Rise.
				Products.	
0 to 1%	1100°	641	715	15.04	42.9°
1 " 2%	1142.5°	670	686	15.31	40°
2 " 3%	1182°	694	662	15.58	37°
3 " 4%	1219°	722	634	15.85	35°
4 " 5%	1254°	742	614	16.12	33°
5 " 6%	1287°	768	588	16.39	31°

<i>FeS</i> <i>Oxidized.</i>	<i>Temp.</i> <i>at</i> <i>Start.</i>	<i>Heat</i> <i>Absorbed</i> <i>by Air.</i>	<i>Net</i> <i>Heat</i> <i>Available.</i>	<i>Calorific</i> <i>Capacity</i> <i>of</i> <i>Products.</i>	<i>Temp.</i> <i>Rise.</i>
6 " 7%	1318°	789	567	16.66	29°
7 " 8%	1347°	809	547	16.93	27°
8 " 9%	1374°	823	533	17.20	26°
9 " 10%	1405°	847	509	17.47	24°
At 10%	1429°

There is no object in extending above table, because it is constructed on the particular assumption that radiation losses would amount to 5° during the burning out of 1 per cent of FeS. This quantity would evidently vary with the size of the converter, the amount of matte being treated and the speed of blowing, because as the contents become hotter their rate of cooling would be increased. The object of the above table, so far as it went, was to show that 47.5° was the theoretical rise for the first 1 per cent, but that the theoretical rises for succeeding per cents would be less and less; in such manner, instead of rising $(47.9 - 5) \times 10 = 429^\circ$ for an oxidation of 10 per cent of FeS the actual rise figures out only 329°.

One of the most necessary data which is badly needed for these converters, and in fact for Bessemer converters in general, is the heat loss by radiation and conduction, in other words, how much heat would be lost by the charge if simply standing still, how much would the temperature of a given charge fall per minute if standing still. This could be easily obtained by running in a charge of pretty hot matte, and following its temperature curve as it cools, without any necessity of letting it freeze, but merely starting up the blast when the rate of cooling has been satisfactorily determined. If these determinations were coupled with details as to the temperature of the outside air, its velocity of impingement against the converter, the temperature of the outside shell, the area of radiating surface and the thickness of the lining, we would soon get data with which to render entirely definite and exact the whole thermal investigation of a "Bessemerizing" operation. This should be supplemented by analyses of the gases during the blow and the temperature curve of the contents as the blow

progresses. Scientific metallurgists must, at present, simply assume many of these data, because of lack of them. We are looking to the metallurgical directors of copper plants for some of this badly-needed technical data.

Problem 110.

W. Randolph Van Liew (*Trans. Am. Inst. Mining Eng.*, 1904, p. 418) gives the following analyses of a charge of matte blown to blister copper in a Bessemer converter:

	<i>Cu.</i>	<i>Fe.</i>	<i>S.</i>	<i>Zn.</i>
Matte.....	49.72	23.31	21.28	1.19
10 minutes.....	50.20	23.15	20.95	1.20
20 "	56.88	17.85	19.74	0.84
30 "	64.60	10.50	18.83	0.70
40 " (last slag skimmed)	76.37	2.40	16.30	0.45
70 " (blister copper)	99.120	0.038	0.159	0.09

	<i>As.</i>	<i>Sb.</i>	<i>Ag.</i>	<i>Au.</i>
Matte.....	0.11	0.14	0.152	0.00055
10 minutes.....	0.09	0.12	0.147	0.00048
20 "	0.08	0.10	0.176	0.00069
30 "	0.08	0.13	0.191	0.00083
40 " (last slag skimmed)	0.08	0.13	0.240	0.00110
70 " (blister copper)	0.0012	0.006	0.312	0.00111

The percentage composition does not exhibit clearly the relative time and amount of the elimination of impurities, because of the varying weight of the bath.

Required:

(1) Assuming 1,000 kilograms of matte to be treated, find the weight of the matte at each period of the blow.

(2) The loss of each constituent of the bath during each period.

(3) The heat evolution during each period.

(4) The loss of heat per minute due to radiation and conduction, assuming that the heat starts with matte at 1,100° and ends with blister copper at 1,200°, and that 1 per cent of copper (reckoned on the matte) is oxidized during the last period.

(1) The first question is to find some constituent of the matte whose weight does not vary during the blow, to serve as a basis for the calculations. If the analyses be taken as reliable in all details (we can make no other assumption) we see that there is very little loss of anything in the first 10 minutes, evidently because of the low temperature of the matte. Afterwards, iron falls off rapidly, also sulphur and zinc, while silver and gold increase in percentage, because of the falling off in weight of the bath as a whole. The slag up to the last skimming, contains usually but very little copper; in the last period we are told to assume a loss of 10 kilos of copper by oxidation. The most rational basis for calculating the weight of the bath is to assume the copper contents constant for the first 40 minutes.

Copper in 1000 kg. of matte at starting	=	497.2 kg.
Weight of matte at starting		1000.0 "
" " " 10 minutes = $497.2 \div 0.5020$	=	990.4 "
" " " 20 " = $497.2 \div 0.5688$	=	874.1 "
" " " 30 " = $497.2 \div 0.6460$	=	769.7 "
" " " 40 " = $497.2 \div 0.7637$	=	651.0 kg.
" " metal 70 " = $487.2 \div 0.9912$	=	491.5 "

(1)

From the analyses given, and calling the shortage of percentage in the analyses oxygen, we have the following table of weights and eliminations:

(2)

Per 1000 kg. of Original Matte.

	<i>Cu.</i>	<i>Fe.</i>	<i>S.</i>	<i>O.</i>
Start.....	497.2	233.1	212.8	41.0
<i>Eliminated</i>	0.0	3.8	5.3	0.1
End 10'.....	497.2	229.3	207.5	40.9
<i>Eliminated</i>	0.0	73.3	35.0	2.9
End 20'.....	497.2	156.0	172.5	38.0
<i>Eliminated</i>	0.0	75.2	27.6	—0.3
End 30'.....	497.2	80.8	144.9	38.3
<i>Eliminated</i>	0.0	65.2	38.8	12.0
End 40'.....	497.2	15.6	106.1	26.3
<i>Eliminated</i>	10.0	15.4	105.3	24.9
End 70'.....	487.2	0.2	0.8	1.4

Zn.	As.	Sb.	Ag.	Au.
11.9	1.1	1.4	1.52	0.0055 = 1000.0
0.0	0.2	0.2	0.06	0.0007 = 9.6
11.9	0.9	1.2	1.46	0.0048 = 990.4
4.6	0.2	0.3	-0.08	-0.0012 = 116.3
7.3	0.7	0.9	1.54	0.0060 = 874.1
1.9	0.1	-0.1	0.07	-0.0004 = 104.4
5.4	0.6	1.0	1.47	0.0064 = 769.7
2.5	0.1	0.2	-0.09	-0.0008 = 118.7
2.9	0.5	0.8	1.56	0.0072 = 651.0
2.5	0.5	0.8	0.03	0.0017 = 159.5
0.4	0.0	0.0	1.53	0.0055 = 491.5

Our table is not absolutely accurate, as can be seen from an apparent gain in both silver and gold in the periods 10' - 20' and 30' - 40'. This is caused by a loss of copper during those periods, but the amounts of gold and silver are too small to serve as a base for revising the table. If we were to assume the gold as constant it would make a smaller weight of bath at the ends of those periods, but the figures are not reliable enough to make this correction worth while.

The very small total loss in the first 10 minutes and the loss of time thus occasioned, could in all probability be obviated by putting the matte hotter into the converter at the start.

A graphic representation of the course of a blow is usually made by plotting the *percentages* of each element in the bath at given periods. *This plan is largely misleading*; the diagram should be made by plotting the calculated *weights* of each element present at the given period, such as are found in the above table.

(3) The heat evolution is to be found by taking the weights of each element oxidized out, calculating the heat of its oxidation and formation of slag, and subtracting the heat necessary to break up the equivalent amount of its sulphide. The heat necessary to separate the sulphides from each other is unknown.

Period I.—Start to 10'.

Heat of oxidation:

Fe to $\text{FeO} \cdot \text{SiO}_2$
S " SO_2

3.8×1332
 5.3×2164

Cal. Cal.
= 5,062
= 11,469

			<i>Cal.</i>	<i>Cal.</i>
As	"	As ₂ O ₃	0.2×1043	= 209
Sb	"	Sb ₂ O ₃	0.2×695	= 139
				<hr/> 16,879

Decomposition of sulphides:

Fe	from	FeS	3.8×429	= 1630
As	"	As ₂ S ₃	0.2×2000 (?)	= 400
Sb	"	Sb ₂ S ₃	0.2×1433	= 287
				<hr/> 2,317

Net heat evolution	<hr/> 14,562
--------------------	--------------

The other periods are similarly calculated, and yield the following results:

	<i>Start-10'</i>	<i>10'-20'</i>	<i>20'-30'</i>	<i>30'-40'</i>	<i>40'-70'</i>	$\frac{1}{2}$ last.
Heat of oxidation.....	16,879	179,797	162,476	174,316	257,046	85,682
Decomp. of sulphides.....	2,317	35,321	33,719	30,113	10,410	3,470
	<hr/>					
Net heat evolution.....	14,562	144,476	128,757	144,203	246,636	82,212

The last column is added for comparison, being the heat evolution per average 10' in the last period. (3)

(4) The loss of heat by radiation and conduction can be found, as a whole, by assuming the converter body to contain the same heat at finishing as at starting, which is a likely assumption, since the lining loses somewhat in weight but ends up at a higher temperature. Then we know how much heat was in the original matte at 1,100°, how much was generated, how much is in the slag and copper, and can calculate approximately how much is carried out in the gases. These enable us to find, by difference, the loss by radiation and conduction which can then be averaged up per minute.

	<i>Calories.</i>
Heat in 1000 of matte at 1100°	= 214,000
Net heat generated in the blow	= 678,635
	<hr/>
Total available	= 892,635

Heat in 491.5 Copper, at 1200°	= 85,995
" " 424.0 SO ₂ , " 1000°	= 97,020
" " 947. N ₂ , " 1000°	= 248,160
" " 550. Slag, " 1250°	= 187,000
	<hr/>
Heat accounted for	618,175
	<hr/>
Loss by radiation and conduction	= 274,460
Loss per minute, per 1000 kg. matte	= 3,920 (4)

It is thought that the principles explained and the methods of calculation illustrated will suffice to show to copper metallurgists how important information is obtainable by applying the principles of thermochemistry to copper smelting, and to indicate the lines along which experiment and results of measurement and observation are greatly to be desired.

THE ELECTROMETALLURGY OF COPPER.

The electric current is used in metallurgy either for its electrolytic effect or for its electrothermal action. In the former the property of the current utilized is its ability when passing in one direction through an electrolyte, of causing at the cathode a *reducing* action, such as the separation of metal from the electrolyte or the reducing of a ferric salt to a ferrous salt, and at the anode a *perducing* effect, the direct opposite chemically of reducing, such as the taking of a metal into the electrolyte or the perducing of a ferrous or cuprous salt to a ferric or cupric condition. In such a process heat is inevitably generated to some extent by the passage of the current through the ohmic resistance offered by the electrolyte. The extent to which heat is thus generated, coincident with the electrolytic action of the current, is of no significance whatever upon the nature of the process, which remains essentially *electrolytic* as long as the current is used for and performs its electrolytic decomposing function. However, when the heat thus coincidently and inevitably generated in the operation of a process essentially electrolytic, is sufficient to keep melted an electrolyte which is not liquid at ordinary temperatures, the apparatus as a whole may not improperly be regarded as a furnace, and is very properly classed as an *electrolytic furnace*.

Electrothermal processes are those characterized by the absence of electrolysis, as shown by the arrangement and working of the apparatus, use of alternating current, etc., and in which the current is used solely for its heating effects. Such processes are carried on in electric furnaces, and are essentially processes in which chemical reactions or physical changes are brought about in the charge solely by the action of the temperature maintained by the assistance of the electric current. Metallurgically, the furnaces used are resistance furnaces, arc furnaces and combinations of the two. In resistance furnaces the heat operating the furnace is produced through the agency of the resistance of the substance or charge itself, or of a solid, liquid or granular resistor, intermingled with, in contact with, or placed in the neighborhood of the material to be heated. In arc furnaces the current jumps a gap between two poles, and generates locally the very high temperature of the arc, which is utilized by feeding the material to be treated into it or by bringing in close proximity to it. In the combined arc-resistance furnace, the material being treated forms one or both poles of the arc, and is therefore heated by the arc itself as well as by the passage of the current through its own substance.

In electrolytic processes the output of material, or commercial efficiency of the process, is essentially dependent upon the amperage of the current, since electrolytic effects are proportional to the amperes passing through the electrolyte. In electrothermal processes the commercial efficiency of output will vary with the total energy dropped by the current in the furnace, *i. e.*, will be proportional to the watts of current used up, not to its amperage or voltage, but to the product of these. Direct currents only are employed in electrolytic processes; direct or alternating may be used in electrothermal processes, but alternating are preferred, because of the complete absence of one-sided electrolytic effects when they are used.

Assuming familiarity with the ordinary non-electric metallurgy of copper, we may divide the electrometallurgy of copper into the following classes:

I. Electrolytic processes—

1. Direct treatment of ores.
2. Treatment of matte.

3. Extraction from solutions.
4. Refining of impure copper.

II. Electrothermal processes—

1. Direct smelting of ores.
2. Melting and casting of copper.

I.

Electrolytic Processes.

Copper has an atomic weight of 63.6. It occurs chemically as cuprous compounds, formulæ CuA^I , or cupric compounds, formulæ CuA^{II} , where A^I is a univalent or monad acid radicle and A^{II} a bivalent or dyad acid radicle. As a monad atom, copper has a chemical equivalent of 63.6, as a dyad element 31.8. The amounts of copper dissolved into or deposited from a cupric or cuprous salt are proportional to the chemical equivalent of copper in these two states and to the amperes flowing. Assuming that 1 ampere liberates electrolytically 0.00001036 grams of hydrogen per second, we will have as the amount of copper concerned in the passage of 1 ampere through one tank:

	<i>Cuprous Compounds.</i>	<i>Cupric Compounds.</i>
1 Ampere, per second...	0.0006589 grams	0.0003295 grams
per minute ..	0.03953 "	0.01977 "
per hour.....	2.372 "	1.186 "
per day.....	56.93 "	28.46 "
per year.....	20.78 kilograms.	10.39 kilograms

A useful datum to remember, if one is used to working in English measures, is that one ampere deposits practically one ounce avoirdupois (28.35 grams) of copper per day in each cell using cupric compounds, and 2 ounces for cuprous compounds, or, respectively, one-sixteenth and one-eighth of a pound per day. These figures, are of course, the theoretical figures for an ampere efficiency of 100 per cent.

I. 1.—TREATMENT OF ORES BY ELECTROLYSIS.

There are no native ores of copper susceptible of being melted and electrolyzed—in the manner for instance, that sodium nitrate (Chili saltpeter) can be melted and electrolyzed for the production of sodium. The most abundant ore of copper, its

sulphide, occurs mostly mixed with several times its weight of foreign material, and even if picked out pure and melted it redissolves copper at the cathode so actively that no electrolysis is possible. Faraday showed that melted cupric oxide is decomposed by the current; and if the oxides of copper were found anywhere in sufficient purity and quantity they could be melted and decomposed electrolytically, but hardly in any case as cheaply as they can be reduced by carbonaceous material.

Cupric chloride is found in nature as atacamite, with the formula $\text{CuCl}_2 \cdot 3\text{Cu}_2\text{O} \cdot 2\text{H}_2\text{O}$, in a comparatively pure condition, but in small quantity, in Chili. Such material will dissolve in considerably quantity in melted salt (NaCl), and can then be electrolyzed. The dissolved copper salt is first reduced by the current, with evolution of chlorine, to CuCl , and then this decomposed. The quantity of this material is at present insignificant, but there is a possibility of an electrolytic process along this line.

Cuprous chloride does not occur in nature, but can be readily made from other copper-bearing material. Chlorine gas, for instance, converts the common copper sulphide, Cu_2S , into CuCl (Ashcroft's process). When melted, cuprous chloride conducts the current very well, copper separating out as fine leaves. The melt cannot be heated to the melting point of copper and the copper obtained liquid, because it vaporizes too easily. It is a good conductor, its resistivity at 50° above its melting point being only 6 ohms (per centimeter cube).

Problem 111.

In electrolyzing a bath of melted cuprous chloride, using an unattackable anode, the electrodes are 4 centimeters apart, and a current density of 0.5 amperes per square centimeter is used.

Required:

- (1) The voltage required for running the bath.
- (2) The proportion of the energy of the current converted into heat.
- (3) The volume of chlorine, at 0° , liberated per minute by a current of 1,000 amperes.
- (4) The output of copper in kilograms per kilowatt-hour of electric energy employed.

Solution:

(1) The voltage required includes that necessary to overcome the ohmic resistance of the electrolyte plus that absorbed in chemical decomposition. With a resistivity of 6 ohms, current density 0.5 amperes per square centimeter, and distance between electrodes 4 cm., the first item is

$$V^c = 6 \times 0.5 \times 4 = 12$$

The second item comes from the heat of formation, by dividing that heat expressed per chemical equivalent by 23,040. Since $(\text{Cu, Cl}) = 35,400$ Calories, we have

$$V^d = 35,400 \div 23,040 = 1.5$$

The total voltage required would be

$$V^c + V^d = \mathbf{13.5} \text{ volts.} \quad (1)$$

This is independent of drop of voltage at contacts of electrodes with the conductors. That may amount to 0.5 or 1.0 volt, unless the contacts are very closely looked after.

(2) The current drops as sensible heat:

$$12 \div 13.5 = 0.89 = \mathbf{89} \text{ per cent of its energy.} \quad (2)$$

(3) Assuming 100 per cent efficiency of liberation of chlorine, we have:

Hydrogen gas liberated by 1 ampere, in 1 sec. = 0.00001036 gr.

Chlorine gas liberated by 1 ampere, in 1 sec.

$$0.00001036 \times 35.5 \text{ (Chem. eq. wt.)} = 0.0003677 \text{ "}$$

Chlorine gas per 1000 amperes in 1 minute = 22.06 "

Volume of chlorine, at 0° C.

$$22.06 \div (0.09 \times 35.5) = \mathbf{6.9} \text{ litres.} \quad (3)$$

(4) One kilowatt, at 13.5 volts, gives $1000 \div 13.5 = 74$ amperes. This current, in one hour, will furnish, at 100 per cent efficiency

$$2.372 \times 74 = \mathbf{175} \text{ grams of copper.} \quad (4)$$

Lower current densities would absorb less voltage and give a greater power-factor output.

I. 2—ELECTROLYTIC TREATMENT OF MATTE.

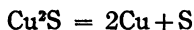
Matte is a mixture of Cu_2S with FeS , and frequently impure with Pb , Zn , Ag , Au , As , Sb , Ba , etc. It melts sharply at about $1,000^\circ \text{C.}$, to a thin liquid; it sets quickly to a hard, stony mass. When melted it can dissolve copper rapidly, so that electrolysis results in the matte being re-formed as quickly as it tends to be decomposed, and it apparently conducts the current without decomposition. If it could be dissolved in certain other fused sulphides in small amount, such as in fused sodium sulphide, it could conceivably be electrolyzed continuously, but no process has as yet been developed along these lines. If it could be dissolved in aqueous solutions of alkaline or other sulphides, it might be electrolyzed in such solvents, but no successful solvent of this nature has been found. It is not impossible that some aqueous solutions may be found to answer this purpose.

Solid matte is conducting, and may be used as an anode or a cathode. When so used it is acted upon by the electric current, reducingly as cathode and perducingly as anode; that is, used as cathode it tends to be reduced *in situ* to metallic copper and iron, if there is any base present capable of uniting with and carrying away the sulphur; used as anode its copper tends to pass into combination with the acid radicle of the electrolyte, leaving the sulphur behind.

USE OF MATTE AS ANODE.

This has appeared to many persons a hopeful application of electrometallurgy to copper. The matte is cast around some strips of copper, or copper netting is better, these giving the piece strength, preventing its disintegrating too quickly, and serving as conductors. Used in acidulated copper sulphate solution, the tendency is to dissolve out copper as copper sulphate and leave the sulphur as a residue. The latter is a non-conductor, forming an insulating layer, which increases greatly the voltage required to run the bath. Attempts to scrape off this layer are fruitless, because of the irregular, cavernous corrosion of the anodes. Marchesi, an Italian, installed a plant to work this process near Genoa in 1882; a plant was also erected in Stolberg, Germany, Both were subsequently abandoned as impracticable.

The theoretical reaction is for purest matte

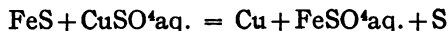


so that for four chemical equivalents of copper deposited one molecule of Cu_2S is broken up. The voltage corresponding to the chemical work done is, therefore,

$$\frac{20,300 \div 4}{23,040} = 0.22 \text{ volt.}$$

The voltage required by the cell is this plus that absorbed in overcoming the ohmic resistances of the circuit.

If the matte were only FeS , the reaction would consist in the solution of iron, sliming of sulphur, and deposition of an equivalent amount of copper:



and the energies involved are

(Fe, S)	=	24,000	Calories absorbed
(Cu, S, O^4 , aq.)	=	197,500	" "
(Fe, S, O^4 , aq.)	=	234,900	" evolved
Sum	=	13,400	" "

and the voltage *contributed* to the circuit is

$$\frac{13,400 \div 2}{23,040} = 0.29 \text{ volt.}$$

If the matte is, as it usually is, part Cu_2S and part FeS , then when it is uniformly corroded there occurs a combination of the above two reactions. If the matte corresponded, for instance, to the formula $\text{Cu}_2\text{S.FeS}$, and these were simultaneously acted upon, the current would be divided in the proportions required by the preceding reactions; that is, twice as much to handle the Cu_2S as for the FeS . The voltages concerned will enter into the calculation in the proportions 2 to 1, and the calculated voltage of decomposition will be

$0.22 \times \frac{2}{3} =$	0.147	volt absorbed.
$0.29 \times \frac{1}{3} =$	0.097	" contributed.
Sum =	0.05	" absorbed.

The calculation can be made for any proportions of Cu_2S and FeS , remembering that every 159.2 parts of Cu_2S require twice as much current as 88 parts of FeS .

Problem 112.

Marchesi erected and operated for some time an electrolytic plant using copper matte as anodes. The matte used contained 30 per cent copper, 30 sulphur and 40 iron, and the anodes measured $800 \times 800 \times 30$ mm., and weighed 125 kilograms. The cathodes were $700 \times 700 \times 0.3$ mm. The tanks were lead lined, with interior dimensions $2,000 \times 900$ mm. \times 1,000 mm. deep. Electrolyte an acid solution of copper and iron sulphates. Resistivity assumed at 6 ohms. The plant contained 120 tanks, arranged in ten groups of twelve each, each group being run by a separate dynamo. Current density, 30 amperes per sq. meter of cathode surface; each tank contained twenty anodes and twenty-one cathodes. Conductors, 30 mm. diameter; total length to one group 10 meters.

Required:

- (1) The electrical current required by each group of twelve tanks and the motive power to run its dynamo.
- (2) The rate at which the anodes lost weight per day.
- (3) The rate at which FeSO_4 accumulates in the bath, in per cent of the weight of the bath.
- (4) The output of copper per day.
- (5) The length of time necessary to plate 1 cm. thickness of copper on one side of each cathode plate.

Solution:

(1) The first point to be solved is the voltage required per tank, and that consists of voltage absorbed by ohmic resistance and that of chemical decomposition. The first must be found from the ohmic resistance of the baths, the second from the chemical reactions involved.

With twenty anodes, each 30 mm. thick, and twenty-one cathodes (the end ones against the ends of the tank) 0.3 mm. thick, the thickness of electrodes in a tank is

$$\begin{aligned}(20 \times 30) + (21 \times 0.3) &= 606.3 \text{ mm.} \\ &= 60.6 \text{ cm.}\end{aligned}$$

and the free space between, in the length of the tank, is

$$200.0 - 60.6 = 139.4 \text{ cm.}$$

Since this is divided into 40 spaces, the free space is

$$139.4 \div 40 = 3.5 \text{ cm.}$$

The total anode surface is, assuming them entirely immersed,

$$80.0 \times 80.0 \times 2 \times 20 = 256,000 \text{ sq. cm.}$$

and of the cathodes,

$$70.0 \times 70.0 \times 2 \times 20 = 196,000 \text{ sq. cm.}$$

giving current passing through a tank

$$19.6 \times 30 = 588 \text{ amperes.}$$

Since the tank is wider and deeper than the plates, the effective cross-sectional area of electrolyte is 25.6 sq. m. at the anode surface, 19.6 sq. m. at the cathode surface, and greater than either (by spreading of current lines) in between. It will not be far wrong, under these conditions, to take the effective area of the electrolyte as about that of the larger electrode, viz., at 25.6 sq. m. The resistance of the tank thus becomes

$$R = \frac{6 \times 3.5}{256,000} = 0.000082 \text{ ohm.}$$

and the voltage absorbed in overcoming ohmic resistance

$$0.000082 \times 588 = 0.048 \text{ volt.}$$

During active corrosion, if copper and iron are dissolved in the proportions 30 to 40, this would be, in chemical equivalent

proportions as	$30 \div 31.8$ to $40 \div 28$
or as	0.943 to 1.429

since the current divides, in doing mixed electrolysis, in proportion to the number of chemical equivalents dissolved or deposited. It thus results that $0.943 \div (0.943 + 1.429) = 0.4 = 40$ per cent of the current is dissolving copper and 60 per cent dissolving iron. The corresponding voltage of the chemical work is, therefore,

$$0.22 \times 0.40 = 0.088$$

$$0.29 \times 0.60 = - 0.174$$

$$\text{Sum} = - 0.086 \text{ volt.}$$

The sum of these two voltages is

$$V^c = 0.048 \text{ volt}$$

$$V^d = - 0.086 \text{ "}$$

$$V = - 0.038 \text{ "}$$

The conclusion is, that as long as the surface of the matte is clean, and no resistance offered by the non-conducting sulphur slime, the bath will really require no outside current to run it, but will practically run itself. The resistance of connections would absorb the small excess of voltage produced. This is as far as calculation can go. Practical experience with the bath records that the voltage required quickly rose to 1 volt, and after a few days running reached 5 volts. It is practically certain that this was caused entirely by the non-conducting film formed on the anodes.

(2) With 588 amps. passing, and 40 per cent dissolving copper, or 235 amps., the copper dissolved per day in one tank is

$$\begin{aligned} 28.46 \times 235 &= 6688 \text{ grams} \\ &= 6.688 \text{ kilograms} \end{aligned}$$

and the weight of matte dissolved per day

$$6.688 \div 0.30 = 22.3 \text{ kilograms.}$$

Since the 20 anodes in a tank weigh $20 \times 125 = 2500$ kilograms, their loss of weight per day is

$$22.3 \div 2500 = 0.009 = 0.9 \text{ per cent} \quad (2)$$

and to lose their whole weight would theoretically require

$$100 \div 0.9 = 111 \text{ days.}$$

Practically, the plates went to pieces in about half that time, when about one-half of their weight had been dissolved.

(3) The iron dissolved is 40 per cent of the matte decomposed, or 8.9 kilograms per day. This forms

$$8.9 \times \frac{152}{56} = 24.2 \text{ kg. FeSO}_4.$$

The tank is not quite full of solution, but say to within 3 cm. of the top. This gives a space of

$$\begin{aligned} 200 \times 90 \times 97 &= 1,746,000 \text{ cc.} \\ &= 1.746 \text{ cu. m.} \end{aligned}$$

From this would be deducted the volume of the electrodes:

$$\begin{aligned} 80 \times 80 \times 3 \times 20 &= 384,000 \text{ cc.} \\ 70 \times 70 \times 0.3 \times 21 &= 34,300 \text{ "} \\ \hline \text{Sum} &= 418,300 \text{ "} \\ &= 0.418 \text{ cu. m.} \\ \text{Volume of solution} &= 1.328 \text{ "} \end{aligned}$$

Assuming its specific gravity as 1.2, the weight of solution in a tank is

$$1,328 \times 1.2 = 1594 \text{ kilograms}$$

and its content of FeSO_4 is increased per day

$$24.2 \div 1594 = 0.015 = 1.5 \text{ per cent.} \quad (3)$$

The total salts present in the electrolyte, however, do not increase quite that fast, for since 16.73 kg. of copper are deposited per day and only 6.67 kg. are dissolved, the electrolyte loses copper at the rate of 10.06 kg. per day, equal to 25.24 kg. of CuSO_4 per day, which is 1.6 per cent of the weight of the electrolyte. We may, therefore, say that the electrolyte would lose 1.6 per cent of its weight of CuSO_4 per day and gain 1.5 per cent of FeSO_4 —amounting to a virtual displacement of CuSO_4 by FeSO_4 until the copper was all removed. This would result in not many days running before the electrolyte would have to be replaced.

(4) We have previously calculated for one tank, that 16.73 kg. of copper is deposited per day. This amounts for the whole plant to

$$16.73 \times 120 = 2008 \text{ kilograms.} \quad (4)$$

Of this amount, however, only $6.67 \times 120 = 800$ kg. came from the matte, and the rest from the solution. Ample means

must therefore be provided to supply fresh CuSO_4 solution, which was obtained by Marchesi from the roasting and leaching of ore.

(5) Precipitated copper has a density of 8.9. One amp. precipitates per day 28.46 grams. One amp. per square centimeter would therefore deposit in a day

$$\frac{28.46}{8.9} = 3.2 \text{ cubic cm.}$$

$$= 3.2 \text{ cm. thickness.}$$

But the current density used for depositing by Marchesi was only 30 amps. per square meter, = 0.003 amps., per square centimeter, which would deposit a layer per day of

$$\begin{aligned} 3.2 \times 0.003 &= 0.0096 \text{ cm.} \\ &= 0.096 \text{ mm.} \end{aligned}$$

To deposit a layer 1 cm. thick would therefore require

$$1.0 \div 0.0096 = 104 + \text{days.} \quad (5)$$

This is a much slower rate of deposition than is used at present in copper refining, where 100 to 500 amps. per square meter (9 to 45 amps. per square foot) are used. Low-current density deposits purer copper and absorbs less power, but gives a smaller output for a given installation, with consequent higher interest charges, labor costs, amortisation and general expenses.

USE OF MATTE AS CATHODE.

Pedro G. Salom describes the use of this principle, called by him cathodic reduction, and has applied it on a large scale to the reduction of PbS concentrates, used as cathode in dilute sulphuric acid, to spongy lead. If the process is applied to granulated copper matte, assumed as nearly pure Cu_2S to simplify this discussion, the anode product is O_2 gas, and the cathode product H_2 gas mixed with varying quantities of H_2S . A. T. Weightman (*Transactions American Electrochemical Society*, II (1902), p. 76) gives details of such an experiment.

Problem 113.

Fifteen grams of Cu^2S were used as cathode in a 5 per cent solution of H^2SO^4 , using an unattackable antimonial-lead anode. A current of 3.6 amps. was sent through for 3 hours (voltage not given). Area of electrodes 50 sq. cm. each, distance apart 4 cm. Gases contained H^2 and H^2S in the following proportions:

	H^2	H^2S
At 5'	42.4	57.6
At 180'	90.8	9.2
Average 0-180'	79.5	20.5

Required:

- (1) The voltage required to run the cell, if H^2S alone were liberated, 100 per cent pure.
- (2) The voltage required to run the cell at the beginning, at the end, and the average throughout the run.
- (3) The proportion of the Cu^2S reduced to Cu during the run.

Solution:

(1) The voltage to overcome ohmic resistance requires first the resistivity of the electrolyte, which for 5 per cent solution is 4.8 ohms. The ohmic resistance of the cell is, therefore,

$$4.8 \times 4 \div 50 = 0.38 \text{ ohm}$$

and the voltage drop to send 3.6 amperes through this

$$0.38 \times 3.6 = 1.37 \text{ volts.}$$

If H^2S were liberated pure, in which case the solution would be saturated with H^2S , the chemical reactions are



and the energy involved

(Cu^2, S)	= 20,300 absorbed
(H^2, O)	= 69,000 "
(H^2, S)	= 4,800 evolved

$$\text{Sum} = 84,500 \text{ absorbed.}$$

The voltage absorbed in producing this chemical reaction is:

$$\frac{84,500 \div 2}{23,040} = 1.83 \text{ volts}$$

The total voltage necessary to run the cell is

$$1.37 + 1.83 = \mathbf{3.20} \text{ volts.} \quad (1)$$

(2) If no H_2S were formed, and the current liberated only H_2 gas, there would be absorbed in decomposition 1.50 volts, and by the cell as a whole 2.87 volts. Since a molecule of H_2S contains the same amount of hydrogen as a molecule of H_2 , equal volumes of H_2S or H_2 would be liberated by an equal electric current. It follows, therefore, that at 5 minutes 57.6 per cent of the current was performing reduction, liberating H_2S , and 42.4 per cent liberating hydrogen.

The principle here involved in calculating the voltage dropped corresponding to the chemical work done is that of the composition and resolution of voltages, explained by the writer in *Transactions American Electrochemical Society* V. (1904), p. 89. The numerical result desired may be reached in several ways, for instance,

$$\begin{array}{rcl} 1.83 \times 0.576 & = & 1.054 \\ 1.50 \times 0.424 & = & 0.636 \\ \hline & & V^d = 1.69 \text{ volts.} \\ \text{but, for conduction,} & & V^c = 1.37 \text{ "} \\ \hline \text{therefore, total voltage} & & V = \mathbf{3.06} \text{ "} \end{array} \quad (2)$$

At the end of the run we have similarly

$$\begin{array}{rcl} 1.83 \times 0.092 & = & 0.168 \text{ volts} \\ 1.50 \times 0.908 & = & 1.362 \text{ "} \\ \hline & & V^d = 1.53 \text{ "} \\ & & V^c = 1.37 \text{ "} \\ \hline & & V = 2.90 \text{ "} \end{array} \quad (2)$$

For the average running

$$\begin{array}{rcl} 1.83 \times 20.5 & = & 0.375 \text{ volts} \\ 1.50 \times 79.5 & = & 1.193 \text{ "} \\ \hline & & V^d = 1.57 \text{ "} \\ & & V^c = 1.37 \text{ "} \\ \hline & & V = \mathbf{2.94} \text{ "} \end{array} \quad (2)$$

(3) Since 20.5 per cent of the current reduced copper during the run, the weight of copper reduced must have been

$$1.186 \times 3.6 \times 0.205 = 0.88 \text{ grams.}$$

But, the 15 grams Cu_2S contained, if pure,

$$15 \times \frac{127.2}{159.2} = 12 \text{ grams.}$$

Proportion reduced in the three hours

$$\frac{0.88}{12} = 0.073 = \mathbf{7.3} \text{ per cent.} \quad (3)$$

This method of reduction of matte would need radical improvement before there could be any possibility of its commercial application.

I. 3—ELECTROLYTIC EXTRACTION FROM SOLUTIONS.

This branch of the subject covers some promising processes which have not, however, been as yet practically successful. Their consideration, however, from a quantitative point of view, is not devoid of interest or lacking in instruction.

The waters of many copper mines carry copper sulphate, produced from the weathering and leaching of copper sulphide ores. The solutions are generally too dilute to allow of concentration and crystallizing out to blue vitriol. The standard method of treatment is to pass the solutions over pig iron or scrap iron, thus precipitating the copper as a sort of metallic mud called "cement copper," which contains much iron, besides the impurities of the iron used, so that it is sometimes only 90 per cent down to 60 per cent copper. This precipitate needs a strong refining to bring it up to merchant copper, with considerable loss of copper in the operation.

Two electrolytic methods are applicable to the treatment of such solutions: 1. The use of soluble iron anodes. 2. The use of insoluble anodes.

(1). *Use of Soluble Iron Anodes.*

If iron in plates or sheets, or bundles of scrap iron in a crate or holder are immersed in copper sulphate solution and simultaneously connected electrically with a copper plate to serve

as cathode, no copper precipitates on the iron, but all is precipitated on the copper. The iron acts as a soluble anode, going into solution as ferrous sulphate, while the copper is deposited out passive, dense, and practically chemically pure, on the cathode sheet. Since more energy is developed by the solution of the iron than is absorbed in the deposition of the copper, there is electromotive force generated by the chemical action, which will run the tank like a short-circuited battery cell, if the iron and copper are simply connected by a low resistance wire. This electromotive force will send a current of a certain amount through the cell, depending on its internal ohmic resistance plus the resistance of the external conductor. If it is desired to force matters, and to precipitate the copper faster than this auto-precipitation, an impressed electromotive force from a dynamo may be put on and the cell made to work faster.

Problem 114.

A copper sulphate solution whose resistivity is 50 ohms is run for precipitation through tanks, each of which contains fifteen anodes of cast iron 40 x 80 cm. in size, and sixteen sheets of copper of similar size, the distance between averaging 5 cm. The anodes and cathodes are short-circuited by resting on a triangular copper distributing bar of negligible resistance. Assume resistance of contacts to be such that 0.1 volt will be lost at them.

Required:

- (1) The electromotive force generated by the chemical action.
- (2) The total current operative in each tank, and the current density.
- (3) The weight of copper deposited in each tank per day.
- (4) The weight of iron dissolved in each tank per day.

Solution:

(1) From the thermochemical tables (Metallurgical Calculations, Part I. p. 24) we have:

$$\begin{array}{rcl} (\text{Fe, S, O}^4, \text{aq.}) & = & 234,900 \text{ Calories} \\ (\text{Cu, S, O}^4 \text{ aq.}) & = & 197,500 \quad " \end{array}$$

$$\text{Excess of anode energy} = 37,400 \quad "$$

Since this is generated for each atom of copper deposited and of iron dissolved, the excess energy per chemical equiva-

lent concerned is $37,400 \div 2 = 18,700$ Calories, and the total electromotive force developed is

$$18,700 \div 23,040 = \mathbf{0.81} \text{ volt.} \quad (1)$$

(2) The loss of voltage at the contacts being 0.1 volt, there is 0.71 volt operative to overcome the ohmic resistance of the solution. From the data given, the fifteen anodes operating on both sides, sandwiched between sixteen cathodes, give

$$15 \times 2 \times 40 \times 80 = 96,000 \text{ sq. cm.}$$

active electrode surface, and taking this as the cross-section of the electrolyte between, we have its resistance as

$$50 \div 96,000 \times 5 = 0.0026 \text{ ohm,}$$

the total current passing in the tank

$$0.71 \div 0.0026 = \mathbf{273} \text{ amperes,} \quad (2)$$

and the current density

$$\begin{aligned} 273 \div 9.6 &= \mathbf{28.4} \text{ amperes per square meter} \\ &= \mathbf{2.6} \text{ amperes per square foot.} \end{aligned} \quad (2)$$

(3) Copper deposited in the tank per day:

$$\begin{aligned} 28.46 \times 273 &= 7770 \text{ grams} \\ &= \mathbf{7.77} \text{ kilograms} \\ &= \mathbf{17.13} \text{ pounds.} \end{aligned} \quad (3)$$

(4) The iron going into solution will be to the copper dissolved as 56 to 63.6. If the iron is cast iron, this may be only 90 to 93 per cent of the loss of weight of the anodes, because they contain only that percentage of iron. If wrought iron or steel sheets are used, the iron dissolved would represent 99 to 99.8 per cent of the loss of weight of the anodes. The iron dissolved per day is

$$\begin{aligned} 7.77 \times 56 \div 63.6 &= \mathbf{6.84} \text{ kilograms} \\ &= \mathbf{15.08} \text{ pounds.} \end{aligned} \quad (4)$$

Problem 115.

One hundred tanks of the kind described in Problem 114 are arranged in a series, the anodes in each tank, however, connected as one large anode, and the cathodes in each as one

large cathode. A dynamo is connected to the series capable of maintaining 110 volts across its terminals. The bus-bars provided are altogether 280 meters long, and are 1×4 cm. in cross-section, of pure copper. All other details of the tanks are as before: resistance of contacts being $0.1 \text{ volt} \div 273 \text{ amps.} = 0.0004 \text{ ohm.}$

Required:

- (1) The ohmic resistance of the bus-bars.
- (2) The current operative in the circuit, and the current density.
- (3) The weight of copper deposited in each tank per day.

Solution:

(1) The conductivity of copper, in reciprocal ohms, is 600,000; its resistivity $1 \div 600,000 = 0.00000167$ ohms. This is its resistance per centimeter cube. The resistance of the bus-bars is therefore

$$0.00000167 \times 28000 \div 4 = \mathbf{0.0117} \text{ ohm.} \quad (1)$$

(2) The total voltage operative in the circuit is the self-generated voltage of 100 tanks, plus the 110 volts from the dynamo, or

$$(0.81 \times 100) + 110 = 191 \text{ volts.}$$

The total resistance of the circuit is that of the 100 tanks, plus 100 sets of connections, plus that of the bus-bars

$$(0.0026 \times 100) + (0.0004 \times 100) + 0.0117 = 0.3117 \text{ ohm.}$$

The total current flowing will therefore be

$$191 \div 0.3117 = \mathbf{618} \text{ amperes} \quad (2)$$

and the current density

$$\begin{aligned} 618 \div 9.6 &= \mathbf{64.4} \text{ amperes per square meter} \quad (2) \\ &= \mathbf{5.9} \text{ amperes per square foot.} \end{aligned}$$

$$\begin{aligned} (3) \quad 28.46 \times 618 \div 1000 &= \mathbf{17.59} \text{ kilograms per day} \quad (3) \\ &= \mathbf{38.79} \text{ pounds per day.} \end{aligned}$$

(2). *Use of Insoluble Anodes.*

If insoluble anodes are used, the copper may be extracted *en masse* from such solutions, and its acid left behind. In such operations, the choice of an anode is not easy. Graph-

itized carbon plates are unattacked, and have practically no back electromotive force; high-silicon iron plates are also said to be very resistant, and pure silicon itself resists still better, but introduces considerable ohmic resistance. Sheet lead anodes become coated with a brown coating of PbO^2 , which is permanent and evolves oxygen freely. Many other substances may possibly be used as anodes; not many practical results of such tests have been published. When operating thus, the electrolyte offers practically the same ohmic resistance as before, averaging probably a little less, and the chemical reaction absorbs energy. The resulting acidified solution may be utilized for dissolving easily-attacked copper compounds from fresh quantities of raw or roasted ore.

Problem 116.

An electrolytic depositing plant treats dilute copper sulphate solution containing 318 grams of copper per cubic meter as CuSO^4 , and its copper is deposited by passing through tanks having insoluble anodes, electrodes 3 centimeters apart, and current density of 20 amps. per square meter. With good circulation, copper is precipitated with no evolution of hydrogen until the precipitation is practically complete. By having many tanks in series the current passing is kept very nearly constant at 300 amps. Each tank contains 1.5 cu. m. of electrolyte.

Required:

- (1) The voltage absorbed in the chemical reaction when precipitating copper, and when the copper is all precipitated.
- (2) The voltage absorbed in overcoming the ohmic resistance of the electrolyte at starting and at the end of the precipitation.
- (3) The total voltage across the electrodes of a tank, at the beginning of the precipitation, just before the last of the copper is precipitated and after all copper is precipitated.
- (4) The time required to precipitate the copper from a batch of solution.
- (5) The output of copper per average kilowatt-hour of electric energy used, adding 0.2 volts to the potential across the electrodes for loss in contacts and bus-bars per tank.

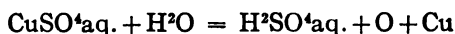
Solution:

- (1) When precipitating copper, we destroy $\text{CuSO}^4\text{aq.}$ and form the corresponding $\text{H}^2\text{SO}^4\text{aq.}$ Their heats of formation being

$$(\text{Cu, S, O}^4, \text{aq.}) = 197,500 \text{ Calories}$$

$$(\text{H}^2, \text{S, O}^4, \text{aq.}) = 210,200 \quad "$$

and since the reaction is



we have to supply

$$(\text{Cu, S, O}^4, \text{aq.}) = 197,500 \text{ Calories}$$

$$(\text{H}^2, \text{O}) = 69,000 \quad "$$

$$\text{Total} = 266,500 \quad "$$

$$\text{and get back } (\text{H}^2, \text{S, O}^4, \text{aq.}) = 210,200 \quad "$$

$$\text{therefore supplying net} = 56,300 \quad "$$

and voltage absorbed in decomposition

$$\frac{56,300 \div 2}{23,040} = 1.22 \text{ volts.} \quad (1)$$

When the copper is all deposited, then only H^2 and O appear at the electrodes, so that the voltage absorbed in decomposition becomes

$$\frac{69,000 \div 2}{23,040} = 1.50 \text{ volts.} \quad (1)$$

(2) At starting, the solution contains

$$318 \times \frac{159.6}{63.6} = 798 \text{ grams}$$

of CuSO^4 per cubic meter, and since the cubic meter weighs at 15° practically the same as water, *i.e.*, 999.1 kg., our solution is

$$\frac{798 \div 1000}{999.1} = 0.08 \text{ per cent } \text{CuSO}^4$$

$$\text{and also equals } 0.798 \div \frac{159.6}{2} = 0.01 \text{ normal.}$$

At the end of the electrolysis the 0.01 normal CuSO^4 solution becomes a 0.01 normal H^2SO^4 solution. The resistivities of both these solutions can be found at once from electrochemical

tables (*e.g.*, Kohlrausch, in Landolt-Bornstein-Meyerhoffer's Tabellen).

With a current density of 20 amps. per square meter (0.002 per square centimeter) and a working distance of 3 cm., the corresponding voltages absorbed in overcoming these ohmic resistances will be

$$\begin{aligned} 1395 \times 3 \times 0.002 &= \mathbf{8.37} \text{ volts} \\ 325 \times 3 \times 0.002 &= \mathbf{1.95} \quad \text{“} \quad (2) \end{aligned}$$

(3) The total voltage across the electrodes, assuming the solution to contain no free acid at starting, will be

$$\begin{aligned} \text{at start, precipitating copper:} \quad & 8.37 + 1.22 = \mathbf{9.59} \text{ volts} \\ \text{at close, precipitating last copper:} \quad & 1.95 + 1.22 = \mathbf{3.17} \quad \text{“} \\ \text{at close, evolving hydrogen:} \quad & 1.95 + 1.50 = \mathbf{3.45} \quad \text{“} \end{aligned}$$

(4) Copper present in a tank: $318 \times 1.5 = 477$ grams.
Time required, 300 amperes

$$\begin{aligned} 477 \div (300 \times 0.0003295) &= 4826 \text{ seconds} \\ &= \mathbf{1 \text{ hr. } 20.5 \text{ min.}} \quad (4) \end{aligned}$$

(4) The average voltage consumed in overcoming ohmic resistance will be considerably less than the mean of 8.37 and 1.95 = 5.16 volts, because when the electrolysis is only half completed, and the solution is 0.005 normal in each ingredient, its resistance will be 487 ohms, and not $(1,395 + 325) \div 2 = 860$ ohms, and the corresponding voltage 2.92. This is because sulphuric acid is a so much better conductor than CuSO_4 , that as soon as acid forms the solution becomes much better conducting. If we calculate the resistances and corresponding voltages absorbed in several steps, we would get more accurate results. Without going into the detailed calculation we will take 3.52 as the average voltage, and we then have the average voltage required per tank:

Decomposition	1.22 volts
Resistance	3.52 “
Contacts	0.20 “
Sum	<u>4.94 “</u>

Kilowatts used per tank

$$\frac{4.94 \times 300}{1000} = 1.482 \text{ kw.}$$

Output per tank per hour

$$300 \times 1.186 = 355.8 \text{ grams.}$$

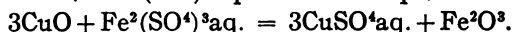
Output per kilowatt-hour

$$355.8 \div 1.482 = 240 \text{ grams.} \quad (4)$$

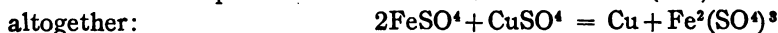
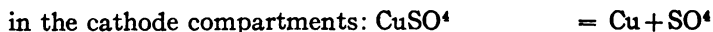
This is, of course, a small output compared with that of a refining process, but it must be remembered that this is an *extraction* process, and its cost is not properly comparable with simple refining but with that of the processes which it replaces, such as precipitation by iron, and with cheap power and expensive iron there may be localities where this method would be economical.

Siemens and Halske invented a combined wet-extraction and electrolytic process, consisting in leaching the roasted copper ore or matte with a solution of ferric sulphate acidulated with sulphuric acid, producing thus a solution of cupric and ferrous sulphates, and then electrolyzing this solution in a cell having an insoluble carbon anode and a diaphragm between the electrodes. The solution is run first through the series of cathode compartments, where its copper is extracted, and back through the anode compartments, where its ferrous sulphate is perduced to ferric sulphate, ready to be used again in leaching ore.

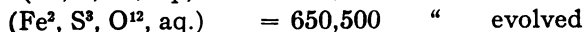
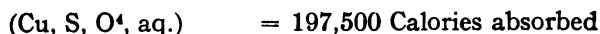
The chemical reactions in leaching ore are



In the electrical precipitation we have:



Confining our calculations to the electrolysis, we have CuSO^4 destroyed and 2FeSO^4 simultaneously perduced to $\text{Fe}^2(\text{SO}^4)^3$, which is then available for re-use in the leaching tanks. The chemical work involved is:



$$\text{Voltage thus absorbed} = \frac{16,800 \div 2}{23,040} = 0.36 \text{ volt.}$$

In addition to this, the voltage necessary to overcome the ohmic resistance of the cell must be counted in.

Problem 117.

An electrolytic tank for working the Siemens-Halske method was of wood, lead lined, 220 cm. long, 100 cm. wide and 100 cm. deep. Each cell contained fifteen anodes and sixteen cathodes, the latter 80 x 80 cm. x 1 mm. The anodes were of carbon rods arranged as a grid 45 cm. x 100 cm. x 1 cm. thick. A porous partition 1 cm. thick was used, the *equivalent* effective free area of which was 0.05. Resistivity of electrolyte in cathode compartment 5 ohms, in anode compartment 8 ohms, partition in middle. Current density 100 amperes per square meter.

Required:

(1) The distance between the diaphragm and each anode and cathode surface, and the resistance of the cell, taking into consideration the contraction of current path due to the diaphragm.

(2) The voltage necessary to run the tank.

Solution:

$$\begin{array}{rcl} (1) & 15 \text{ anodes} \times 1 & = 15.0 \text{ cm.} \\ & 16 \text{ cathodes} \times 0.1 & = 1.6 \text{ " } \\ & & \hline & \text{Sum} & = 16.6 \text{ " } \end{array}$$

Space, anode to cathode

$$\frac{220 - 16.6}{30} = 6.8 \text{ cm.}$$

Space, anode or cathode, to diaphragm

$$\frac{6.8 - 1}{2} = 2.9 \text{ cm.} \quad (1)$$

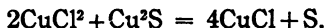
Assume the solution in the diaphragm to have mean resistivity of 6.5 ohms, the equivalent free area being $100 \times 95 \times 0.05 = 475$ sq. cm. (area of diaphragm a trifle less than cross-section of tank). Mean area of electrolyte

cathode compartment	$(6400 + 9500) \div 2 = 7950$ sq. cm.		
anode compartment	$(4500 + 9500) \div 2 = 7000$ " "		
Resistance of			
anode compartment	$8 \times 2.9 \div 7000$	$= 0.0033$	ohm.
cathode compartment	$5 \times 2.9 \div 7950$	$= 0.0018$	"
diaphragm	$6.5 \times 1 \div 475$	$= 0.0137$	"
		<u>0.0188</u>	" (1)

Voltage absorbed, for 64 amperes (to 0.64 sq. m. depositing surface)

$$\begin{array}{rcl}
 0.0188 \times 64 & = & 1.20 \text{ volts} \\
 V^d & = & 0.36 \text{ " } \\
 & & \hline
 V & = & 1.56 \text{ " } \quad (2)
 \end{array}$$

Carl Hoepfner devised a process along similar lines to the above, but based on the use of the two chlorides of copper. A solution of CuCl^2 in brine is used to act upon the ores or roasted matte, dissolving the copper with the formation of CuCl .



The cuprous chloride stays in solution in the brine, and is electrolyzed in tanks containing diaphragms, half the solution going through the cathode compartments, and half through the anode compartments. In the former, copper is precipitated; in the latter, the equivalent amount of chlorine converts the CuCl present into CuCl^2 , which can be used over, mixed with the depleted cathode solution. The total reaction is



and the energy involved

$$\begin{array}{rcl}
 2(\text{Cu, Cl}) & = & 70,800 \text{ absorbed} \\
 (\text{Cu, Cl}^2) & = & 62,500 \text{ evolved} \\
 & & \hline
 \text{Sum} & = & 8,300 \text{ absorbed} \\
 & = & 0.18 \text{ volt.}
 \end{array}$$

Coehn devised a cell for carrying on this process without a diaphragm. The cathode is only half as long as the carbon anode, and the CuCl^2 formed at the latter is so heavy that it sinks to the bottom and is drawn off therefrom, while fresh CuCl solution is quietly poured in above. Since the cathode

does not touch the cupric solution, it is not redissolved thereby, and the two solutions are kept separate.

A great advantage of this process is that Cu is monovalent in CuCl, and therefore twice as much copper is deposited as from CuSO₄ by a given number of amperes.

Problem 118.

Coehn (*Jahrbuch der Electrochemie*, 1895, p. 155) describes his improved partitionless Hoepfner apparatus as containing a copper cathode 100 cm. wide by 50 cm. deep, at a distance of 12 cm. from a carbon anode; solution, 10 per cent NaCl, plus varying amounts of CuCl and CuCl₂. Current density 20 amps. per square meter.

Required:

- (1) The voltage required to run the cell.
- (2) The weight of copper deposited therein per day.
- (3) The weight of copper per kilowatt hour electric power used.

Solution:

- (1) The resistivity of 10 per cent NaCl solution is 8.5 ohms.

$$R = \frac{8.5 \times 12}{5000} = 0.0204 \text{ ohm}$$

V^c , for ohmic resistance = $0.0204 \times 10 = 0.20$ volt

V^d , for chemical reactions 0.18 "

$$V = \text{Sum} = 0.38 \text{ " (1)}$$

$$(2) \quad 28.46 \times 2 \times 10 = 569 \text{ grams per day (2)}$$

$$(3) \quad \frac{569}{24} \times \frac{1000}{10 \times 0.38} = 6210 \text{ grams (3)}$$

$$\frac{569}{24} \times \frac{1000}{10 \times 0.38} = 6.21 \text{ kg.}$$

I. 4. ELECTROLYTIC REFINING OF IMPURE COPPER.

This subject is a large one. It lends itself very well to calculation. It is also comparatively simple in principle. Given a nearly pure copper plate or slab as an anode, in a solution of a copper salt, and a suitable conducting cathode, the metal is simply dissolved and deposited, or is "plated over." The process really consists in extracting copper from the solution at the cathode, and sending it and other soluble impurities into the solution at the anode. The mechanical transportation of the copper, in space, through a distance equal to the space between anode and cathode, is sometimes emphasized as the chief

mechanical work done. It is a real fact that the metal is taken out of the solution at a different spot from where it goes in, but the electric current does not do that transportation—diffusion and circulation are the agents which transport the copper entering the electrolyte at the surface of the anode plate to the surface of the cathode plate, and electric energy does nothing more than create the differences of concentration, which are thus physically neutralized.

The chief expenditure of electrical energy in the refining bath is that converted into sensible heat in overcoming the ohmic resistance of the electrolyte. The other items of electrical work are the overcoming of the ohmic resistance of hangers, rods, bus-bars, clamps and connectors, and the not unimportant resistance of contacts; also the difference of chemical work done in depositing all copper and dissolving part copper and part other impurities; also the chemical work of separating the ingredients of the impure copper, which may be alloyed and have some heat of combination which must be furnished by the current in order to separate them.

Energy Absorbed by the Electrolyte.

The electrolyte is a conductor and absorbs energy according to Ohm's law whenever current passes through it. The solution used in copper refining is almost invariably copper sulphate acidulated with sulphuric acid. The resistivity of copper sulphate, iron sulphate and sulphuric acid solutions, at 20° C., is as follows, in ohms per centimeter cube and ohms per inch cube:

Per Cent in Solution.	<i>CuSO₄</i> .		<i>FeSO₄</i> .		<i>H²SO₄</i> .	
	<i>Ω per cm.³</i>	<i>Ω per inch.³</i>	<i>Ω per cm.³</i>	<i>Ω per inch.³</i>	<i>Ω per cm.³</i>	<i>Ω per inch.³</i>
2.5	92	37
5.	53	21	4.8	1.9
7.5	65	26
10.	31	12	2.5	1.0
15.	24	10	34	14	1.8	0.7
17.5	22	9
20.	1.5	0.6
25.	1.4	0.56
30.	25	10	1.37	0.55

The plain copper sulphate solution is thus seen to be a rather poor conductor, iron sulphate is not so good; sulphuric acid is highly conducting. It is therefore evident that the ohmic resistance of the bath is, for practical purposes, dependent upon its content in free acid; hence the great economic importance of keeping the bath well acidulated. As the bath grows foul with iron sulphate and loses sulphuric acid by formation of insoluble sulphates, chemical solution of slimes, etc., the bath becomes poorer conducting and the energy absorbed in it much greater. A solution in good condition, with 15 to 20 per cent of CuSO_4 and 5 to 10 per cent free H_2SO_4 , may have a resistivity of only 2 to 5 ohms at starting, which may increase to 20 or 25 ohms as the solution becomes impure and the free acid disappears. These facts are of immense importance in the economics of refining.

A comprehensive, systematic study of the resistivities of solutions of various strengths of copper sulphate with various percentages of iron sulphate present and various content of sulphuric acid is greatly needed, and would not be a difficult research to carry out.

Problem 119.

A refining bath is run with a current density of 250 amperes per square meter, with electrodes 4 cm. apart, and starting with electrolyte 15 per cent CuSO_4 and 10 per cent H_2SO_4 . It is run until the sulphuric acid has decreased to 5 per cent.

Required:

- (1) The probable voltage drop across the electrodes at starting.
- (2) The same when the second condition is reached.
- (3) The rate at which the solution would start to rise in temperature at the beginning, ignoring the electrodes.
- (4) The rate, assuming anodes 5 cm. thick and copper cathodes 0.5 cm. thick.

Solution:

- (1) Lacking the experimentally determined datum of the resistivity of the primary solution, we know that it will be somewhere about that of the 10 per cent sulphuric acid solution, viz.: 2.5 ohms. It should be slightly less, because of the copper salt present, and if we assume the conductivity of the solutions

as additive, we would have a conductivity of the mixed solution, in reciprocal ohms as

$$C = \frac{1}{2.5} + \frac{1}{24} = 0.40 + 0.04 = 0.44$$

$$R_{sp} = \frac{1}{0.44} = 2.3 \text{ ohms.}$$

Using this resistivity, the voltage drop across the electrodes, at starting, will be

$$V^c = 2.3 \times 4 \times 0.0250 = \mathbf{0.23} \text{ volts.} \quad (1)$$

(0.0250 amperes goes across each square centimeter and the plates are 4 centimeters apart.)

(2) With H^2SO^4 only 5 per cent, and copper contents, say, 20 per cent, because of solution of copper by free acid, we would have

$$C = \frac{1}{4.8} + \frac{1}{20} = 0.21 + 0.05 = 0.26$$

$$R_{sp} = \frac{1}{0.26} = 3.6 \text{ ohms.}$$

Using this resistivity, the voltage drop is

$$V^c = 3.6 \times 4 \times 0.0250 = \mathbf{0.36} \text{ volts.} \quad (2)$$

In actual practice an increase of 0.01 volt above this might be expected, because of the formation of a film of slime on the surface of the anode.

(3) The solution at starting has a specific gravity of 1.20 and a specific heat of 0.875. (Combination of data from Landolt-Bornstein-Meyerhoffer's Tabellen.) The water value as heat absorber of a column of liquid 1 cm.² and 4 cm. long, between the electrodes, is therefore

$$1.20 \times 4 \times 0.875 = 4.2 \text{ calories per } 1^\circ \text{ C.}$$

Heat equivalent of the electric energy expended

$$0.23 \times 0.0250 \times 0.2389 = 0.00138 \text{ calories per } 1''.$$

Rate of rise of temperature of solution

$$\begin{aligned}
 0.00138 \div 4.2 &= 0.00033^\circ \text{ per second} \\
 &= 0.0198^\circ \quad \text{" minute} \\
 &= 1.2^\circ \quad \text{" hour} \\
 &= 28.8^\circ \quad \text{" day}
 \end{aligned}
 \tag{3}$$

(4) With half the thickness of anode and cathode to be supplied with heat, the copper having a specific gravity of 8.9 and specific heat of 0.093, the water value of the copper concerned per square centimeter area of electrolyte section is

$$\left(\frac{5.0}{2} + \frac{0.5}{2}\right) \times 8.9 \times 0.093 = 2.276 \text{ calories per } 1^\circ$$

Rate of rise of temperature of solution plus electrodes:

$$\begin{aligned}
 0.00138 \div (2.276 + 4.2) &= 0.00021^\circ \text{ per second} \\
 &= 0.013^\circ \quad \text{" minute} \\
 &= 0.78^\circ \quad \text{" hour} \\
 &= 18.7^\circ \quad \text{" day}
 \end{aligned}
 \tag{4}$$

Energy Lost in Contacts.

This is an extremely variable and yet important factor in the economics of copper refining. No one item in copper refining will at the present time better repay close attention and study of methods of improvement. A proper contact should cause a very small voltage drop to begin with, and should be capable of being kept efficient—that is the chief requirement. Contacts are often made on the hit or miss style, and arranged in such position as to receive spattering or drippings from the electrolyte; such may cause immense losses of electrical energy as they rapidly pass from bad to worse.

B. Magnus (*Electrochemical and Metallurgical Industry*, December, 1903), and L. Addicks (*idem.*, January, 1904) have given us valuable information on this point. The weight of the plates, when resting on the contacts, improves the contact; in such cases the anode contacts are best when the tank is first set up and the cathode contacts worst. In such cases a screw clamp, to put several hundred pounds of mechanically applied pressure on the joint, should be adopted, so as to make the contacts "best" all the time.

Figures given by Magnus as a carefully determined average of results in a western refinery are:

Current.....	4,000 amperes		
Current density (per sq. ft.)..	11 "		
Total voltage per tank.....	0.230 volts		
Energy used per tank.....	0.920 kw.		<i>Per</i>
Drop bus-bar to anode rod.	0.0270 volts		<i>Cent.</i>
" anode rod to anode		} = 0.0338 =	14.7
hanger.....	0.0060 "		
" anode hook to anode.	0.0008 "		
" anode to cathode....	0.1782 "	} = 0.1782 =	77.5
" cathode to cathode			
rod.....	0.0045 "	} = 0.0180 =	7.8
" cathode rod to bus-			
bar.....	0.0135 "		
		<hr/>	<hr/>
		0.2300	100.0

It thus appears that in this tank the loss in contacts was some 20 per cent of the total voltage employed (assuming the anode rods to be of such design that their resistance was negligible). Magnus fitted up a similar tank with mercury cup contacts, and found a drop from bus-bar to anode rod of 0.0050 volt instead of 0.0270, and cathode rod to bus-bar 0.0050 instead of 0.0135 volt. If it were possible in the case of above tank to make these improvements alone, the saving on voltage per tank would be 0.0305 volt, or 13.3 per cent of the voltage used, which means a saving of 13.3 per cent of the power required to run the tank.

Problem 120.

In an electrolytic refinery system of 200 tanks the resistance of the contacts was, on an average, 0.0368 volt per tank, and 0.2567 volt across two electrodes; 3,800 amperes was passed through the series, and the voltage at the terminals of the dynamo was 67 volts. Power costs \$157 per kilowatt-year, Efficiency of deposition of copper 82 per cent.

Required:

- (1) The cost of power per ton (2,000 pounds) of copper refined.
- (2) The cost per ton of copper produced, of the power lost

by (a), resistance of the conductor bars (b), by the contacts and (c), consumed in the electrolyte itself.

(3) If interest on capital is 6 per cent, what expenditure would be justified on means for (a), reducing the conductor losses (b), reducing the contact losses (c), reducing the electrolyte losses.

(4) If the ampere efficiency of deposition could be increased 5 per cent by reducing the current density 20 per cent, would it pay?

Solution:

(1) Copper deposited in 1 tank per day

$$3800 \times 0.82 = 3118 \text{ oz.} = 195 \text{ lbs.}$$

In 200 tanks

$$200 \times 195 = 39,000 \text{ "}$$

Power used

$$3800 \times 67 \div 1000 = 255 \text{ kw.}$$

Cost of power per day

$$255 \times \$157 + 365 = \$109.70$$

Cost of power per 2,000 lbs. copper

$$\$109.70 \div 19.5 = \$5.63 \quad (1)$$

(2) The voltage lost in the conductors is

$$67 - 200(0.0368 + 0.2567) = 67 - 58.7 = 8.3 \text{ volts}$$

and the power thus lost

$$3800 \times 8.3 \div 1000 = 31.54 \text{ kw.}$$

$$\text{Cost per year } 31.54 \times \$157 = \$4,952.00$$

$$\text{Cost per day } \$4952 \div 365 = \$13.57$$

$$\text{Cost per ton of copper produced} = \$0.70 \quad (2a)$$

Power lost in the contacts

$$200 \times 0.0368 \times 3800 \div 1000 = 27.97 \text{ kw.}$$

$$\text{Cost, per year} = \$4,391.00$$

$$\text{Cost, per day} = \$12.03$$

$$\text{Cost, per ton} = \$0.62 \quad (2b)$$

Power consumed in the electrolyte

$$200 \times 0.2567 \times 3800 \div 1000 = 195 \text{ kw.}$$

$$\text{Cost, per year} = \$30,615.00$$

$$\text{Cost, per day} = \$83.88$$

$$\text{Cost, per ton} = \$4.30 \quad (3b)$$

(3) The cost of the power lost per year, divided by 0.06, will give the capital investment representing that yearly outlay. This would be

	<i>Cost of Power</i>	<i>Capitalized.</i>
Conductor resistances.....	\$4,952	\$82,530
Contact resistances.....	4,391	73,180
Electrolyte resistances.....	30,615	510,250

In the specific cases in point each 1 per cent of the power consumption which could be saved by improvements of a permanent character, not subject to depreciation, would justify capital expenditures in the plant up to the following amounts:

Conductor resistances.....	\$825
Contact resistances.....	732
Electrolyte resistances.....	5,100

If the improvements were liable to depreciation in use, such as larger tanks, contact clamps, etc., the depreciation must be added to the interest to find the justifiable capital expenditure. Assuming depreciation 10 and 20 per cent, respectively, this plus interest amounts to 16 and 26 per cent, and the justified expenditures must be less than the following amounts for 1 per cent saving of power in each direction:

	10%	20%
	<i>Depreciation.</i>	<i>Depreciation.</i>
Conductor resistances.....	\$309.50	\$190.50
Contact resistances.....	274.50	169.00
Electrolyte resistances.....	1,913.50	736.00

There is here a wide field for experiment and improvement. In the case in point, making all allowances, one would be justified in expending in permanent plant for each tank at least \$1.00 for every 1 per cent reduction which could be made in the power loss in the conductors, \$0.85 for every 1 per cent gained in reducing contact resistances and \$3.68 for each 1 per cent reduction in the resistance of the electrolyte. To be more specific, assume the main conductors to be proportioned to carry 2,000 amperes per square inch of cross-section. Their resistance in the case in point is $8.3 \div 3,800 = 0.0022$ ohm, cross-section 1.9 square inches, resistance per running inch $0.00000067 \div 1.9 = 0.00000035$ ohm, and total length $0.0022 \div 0.00000035 = 6,286$ inches = 524 feet.

The weight, at $62.5 \times 8.9 \div 1,728 = 0.322$ lbs. per cubic inch is

$$6,286 \times 1.9 \times 0.322 = 3,846 \text{ lbs.}$$

which at \$0.20 per lb. costs

$$3,846 \times 0.20 = \$769.20$$

Since there is practically no depreciation (except change in market value) in these copper conductors, if we increased the cross-section of the conductors 100, 200, 300, and 400 per cent, respectively, we would decrease their resistance 50, 67, 75 and 80 per cent, respectively, and arrive at the following figures:

<i>Per Ton of Copper Produced.</i>					
<i>Per Cent</i>		<i>Interest</i>			
<i>Per Cent</i>	<i>Decreased</i>	<i>on</i>			
<i>Increased</i>	<i>Resistance</i>	<i>Increased</i>	<i>Increased</i>	<i>Decreased</i>	
<i>Size of</i>	<i>of</i>	<i>Cost of</i>	<i>Cost of</i>	<i>Cost of</i>	
<i>Conductors.</i>	<i>Conductors.</i>	<i>Plant.</i>	<i>Plant.</i>	<i>Power.</i>	<i>Gain.</i>
100	50	\$769	\$0.0065	\$0.35	\$0.35
200	67	1,538	0.013	0.47	0.46
300	75	2,307	0.019	0.52	0.50
400	80	3,077	0.026	0.56	0.53
900	90	6,923	0.058	0.63	0.57
1,900	95	14,613	0.123	0.67	0.54

We thus see that for this plant, with power costing \$157 a kilowatt-year and copper bar \$0.20 per pound, a great reduction in the power costs up to \$0.57 per ton of copper produced can be made by making the main conductors *ten times* as large; that is, by making them carry only 200 amperes per square inch of section instead of 2,000.

At a locality like Great Falls, Montana, where the water power does not cost over one-tenth the above price, let us say \$15.70 per kilowatt-year, the decreased cost of power, in the above table would be one-tenth the above figures—there would be only \$0.07 per ton of copper to save if all were saved, and it can easily be seen that the gains would be

for 100 per cent increased size.	\$0.029
" 200	" " " "	0.034
" 300	" " " "	0.033
" 400	" " " "	0.030

We reach the maximum saving in this case by increasing the size 200 per cent, giving a current density of 660 amperes per square inch of conductor section.

It can easily be seen that the cost of copper bars, rate of interest, and cost of power are all three factors in determining the economic size to be given the conductors. In general they are made much smaller than they should be because of lack of capital to invest in them. As soon as a refinery is running and paying dividends part of its profits should be applied to permanent investment in heavier copper conductors in order to reduce the running costs.

(4) If the ampere efficiency were increased 5 per cent and the current density 20 per cent, all other data being constant except those affected by these changes, the output of copper would be 87 per cent of the theoretical output of 3,040 amperes instead of 82 per cent of the theoretical output of 3,800 amperes. The output of copper per day would therefore be, in place of 39,000 pounds:

$$3,040 \times 0.87 \times 200 \div 16 = 33,060 \text{ lbs. per day.}$$

The power cost will be reduced 20 per cent by the lower amperage used, that is, be $\$5.63 \times 0.80 = \4.50 per ton—a saving of \$1.13. Whether it will pay to do this depends of what the other fixed charges of the plant are. Decreasing the output 15 per cent increases the fixed charges per ton of copper produced 12 per cent. It is then a question whether 12 per cent of the fixed charges in the first case is greater or less than \$1.13. If the fixed charges amounted to, say, a usual figure of \$5.00 per ton, decreasing the output 15 per cent would increase this charge per ton of copper produced 12 per cent, or \$0.60; but if there is a power saving of \$1.13 there is a margin of \$0.53 per ton in favor of making the change. If the power cost were only \$0.56 per ton of copper it would just barely pay to make the change. Everything depends upon the relative cost of power and of the other fixed charges.

Energy Lost in Conductors.

We have already touched on this subject, but it deserves still greater attention. The resistivity of copper is 0.00000167 ohm per centimeter cube, or 0.00000067 ohm per inch cube.

Given a conductor of certain length its resistance in ohms is 0.00000167 multiplied by its length in centimeters and divided by its cross sectional area in square centimeters. The similar calculation can be made, for the inch units. The drop in potential in the bus-bars is their resistance multiplied by the amperes passing, and the power consumption is the voltage drop into the amperes passing or the resistance in ohms into the square of the amperes passing. The watts thus expended may be expressed in kilowatts, or transposed into horse-power by dividing by 746. The heat generated in the conductors is, per second, in gram calories, the number of watts expended in them multiplied by 0.2389. The rate of rise of temperature of the conductors, leaving out radiation and conduction to the air, will be, per second, the gram calories generated in the conductors divided by the heat capacity of the conductors per degree, which in the case of copper is volume in cubic centimeters into 0.837. This rise in temperature will continue until by radiation and conduction to the air the conductors lose as much heat per second as the current generates in them. This will vary with the shape of the cross section of the conductors, because the loss of heat is proportional to the surface exposed, and the area of exposed surface for a given cross section is greater the thinner the conductor and is a minimum for a round conductor. The amount of heat thus lost can be calculated by the principles explained in Metallurgical Calculations, Part I., pp. 172-186. If it is desired to get along with the minimum heating of the conductors, they should be as flat and thin as possible; if heating can be ignored they may be of the cheap round shape. It should not be forgotten also that the resistivity of copper increases as it gets hotter in direct proportion to its absolute temperature ($C^{\circ} + 273$), so that the heating effect really aggravates itself from this increased resistance.

Problem 121.

A copper conductor is desired to carry 4,000 amperes, 300 meters. Round bars sell at 18 cents per pound. Interest rate 10 per cent. Cost of electric power as delivered \$50 per kilowatt year. Average temperature of surrounding air $20^{\circ} C.$; air still. Conductivity of the copper 600,000 reciprocal ohms per centimeter cube. Specific gravity of copper 8.9, specific heat 0.094.

Aluminium conductors to replace same have conductivity of 375,000 reciprocal ohms, specific gravity 2.60, specific heat 0.230; cost of round bars 36 cents per pound.

Required:

(1) The cross-sectional area of the conductors of copper which will give the minimum cost of power and interest on the investment.

(2) The same for aluminium.

(3) The running temperature of the conductors of copper above the room temperature.

(4) The same for aluminium.

Solution:

(1) Let S = cross section of conductor, in sq. cm.
Resistance of copper conductor

$$0.00000167 \times (300 \times 100) \div S = \frac{0.0501}{S} \text{ ohm.}$$

Power expended in the conductor:

$$\frac{0.0501}{S} \times (4,000)^2 = \frac{801,600}{S} \text{ watts.}$$

Cost of power thus expended, per year

$$\frac{801,600}{S} \div 1,000 \times 50 = \frac{40,080}{S} \text{ dollars.}$$

Weight of copper in conductor:

$$(300 \times 100) \times S \times 8.9 \div 1,000 = 267 \times S \text{ kilograms.}$$

Cost of conductor, if round

$$267. S \times 0.18 \times 2.205 = 106 \times S \text{ dollars.}$$

Interest on cost of conductor, at 10% = $10.6 \times S$ dollars.

Sum of cost of power and interest on investment:

$$\frac{40,080}{S} + (10.6 \times S)$$

Solving for S a minimum, we find $S = 61.5 \text{ sq. cm.}$ (1)

Total costs, substituting S above

$$\$652 \text{ (for power)} + \$652 \text{ (interest)} = \$1,304 \text{ per year.}$$

(2) Resistance of aluminium conductor

$$0.00000267 \times (300 \times 100) \div S = \frac{0.0801}{S} \text{ ohm.}$$

Power expended in the conductor

$$\frac{0.0801}{S} \times (4,000)^2 = \frac{1,281,600}{S} \text{ watts.}$$

Cost of power thus expended, per year

$$\frac{1,281,600}{S} \div 1,000 \times 50 = \frac{64,080}{S} \text{ dollars.}$$

Weight of aluminium in conductor

$$(300 \times 100) \times S \times 2.6 \div 1,000 = 78 \times S. \text{ kilograms.}$$

Cost of conductor, if round

$$78. S. \times 0.36 \times 2.205 = 62 \times S. \text{ dollars.}$$

Interest on cost of conductor, at 10% = $6.2 \times S.$ dollars.

Sum of cost of power and interest on investment:

$$\frac{64,080}{S} + (6.2 \times S.)$$

Solving for $S =$ a minimum: $S = 101.2 \text{ sq. cm.} \quad (2)$ Total costs, substituting S above

$$\$633 \text{ (for power)} + \$627 \text{ (interest)} = \$1,260 \text{ per year.}$$

(3) Power expended in copper conductor

$$\frac{801,600}{61.5} = 13,035 \text{ watts.}$$

Heat generated in conductor, per second

$$13,035 \times 0.2389 = 3,114 \text{ gm. cal.}$$

Area of conductor surface

$$\begin{aligned} & (300 \times 100) \times 3.14 (\sqrt{61.5 \div 0.7854}) = \\ & = 30,000 \times 27.8 \text{ (cm. circumference)} = 834,000 \text{ sq. cm.} \end{aligned}$$

Loss of heat per second by contact with still air, per 1° difference

$$0.000056 \times 834,000 = 46.7 \text{ calories.}$$

Rise of temperature, excluding radiation loss

$$3,114 \div 46.7 = 67^\circ.$$

The radiation loss must, however, be considered. From copper it is 0.00068 gram calories per second per sq. centimeter, if the surroundings are at 0° and the hot body at 100°, this is approximately 0.0000068 gram calories per each degree in this range. We have the combined conduction and radiation losses per 1° per second

$$0.000056 + 0.000007 = 0.000063 \text{ calories}$$

and the rise in temperature of the conductor

$$3,114 \div (0.000063 \times 834,000) = 59^\circ.$$

The conductors would therefore run at a temperature of

$$\begin{aligned} 20 + 59 &= 79^\circ \text{ C.} \\ &= 174^\circ \text{ F.} \end{aligned} \quad (3)$$

A correction of the second order would be to take into consideration the fact that at 79° the copper would have less conductivity than at 20°, its resistivity at 79° being

$$0.00000167 \times \frac{273 + 79}{273 + 20} = 0.0000020 \text{ ohm.}$$

This would make the required section for minimum expense 68 sq. cm. instead of 61.5, and would, by increasing the surface, make a different rise in temperature. The power expended would be the equivalent of 3,373 gram calories per second, and the revised temperature of the conductor would be

$$(3,373 \div 52.54) + 20 = 64 + 20 = 84^\circ \text{ C.}$$

(4) Power expended in the aluminium conductor

$$\frac{1,281,600}{101.2} = 12,665 \text{ watts.}$$

Heat generated in conductor, per second

$$12,665 \times 0.2389 = 3,026 \text{ calories.}$$

Area of conductor in square centimeters = 1,074,000 sq. cm.

Conduction and radiation losses, per 1°

$$(0.000056 + 0.000010) \times 1,074,000 = 70.88 \text{ grm. cal.}$$

Rise in temperature of conductor

$$3,026 \div 70.88 = 43^\circ.$$

Working temperature of conductor

$$43 + 20 = 63^\circ \text{ C.}$$

The aluminium conductor thus is seen to work cooler than the copper, and to admit of a lower minimum of working costs.

Electric Smelting of Copper Ores.

The use of electrothermal processes for smelting copper ores has been proposed in recent years, and in a few cases experimentally tested. The whole question depends on the recognition and appreciation of a few fundamental facts. By far the greater bulk of all copper ores are sulphide ores, and in many cases the sulphur and iron present are sufficient heat producers to allow of the smelting of the ore simply by the heat of their oxidation, if the operation is skillfully conducted. Such is the basic principle of pyritic smelting, and whenever it can be applied it is very economical to do so, and electric processes have no chance of an application.

Other ores of copper contain so small an amount of the metal that the result of the smelting down of the whole to a fluid mass, by any method of fusion, would not repay the cost of the operation. Some such ores can be treated by aqueous and other methods not involving fusion, with a margin of profit to pay for the operation.

The only field for electrothermic processes appears to be in the smelting down of ores carrying too little sulphur to be "pyritically" smelted, and which require, as usually treated, the use of carbonaceous fuel to assist the fusion. Wherever such fuel is expensive, and electric power may be obtained at a low price, an electrothermic process might be theoretically possible and profitable.

Such conditions may easily occur in the vicinity of copper mines. Situated frequently among the mountains, remote from

railways and cheap fuel, they frequently are near large water powers which would furnish cheap electric power. Some may be even so situated that concentration of a very lean sulphide ore to matte by use of fuel, or by mechanical concentration, would be unprofitable, and yet a concentration or simple melting to matte by electrically-generated heat be profitable.

There are, so far as the writer knows, no electrothermal processes yet in commercial operation on copper ores, yet they have been tested experimentally with promising results. Vattier, for instance, conducted experiments at the Livet works of the Compagnie Electrothermique Keller et Leleux, on April 23, 1903, in the presence of several distinguished metallurgists, such as Mr. Stead, of Middlesborough; Mr. Allen, of Sheffield, and Mr. Saladin, of the Creusot works. The ores were Chilean ores sent by the Chilean Government to test the possibility of electric smelting, taken from the "Vulcan" mine, owned by G. Denoso, and low-grade ore from Santiago. At the mines, coke costs \$20 per ton, but the slopes of the Andes afford a fine opportunity for developing large water powers cheaply; it is estimated that the total cost of electric power delivered should not exceed \$6 per kilowatt-year. A detailed account of these tests can be found in the appendix to the Report of the Canadian Commission on Electric Smelting, 1904.

Problem 122.

Vattier mixed his rich and poor Chilean ores to a charge consisting of

	<i>Per Cent.</i>
Copper.....	5.10
Sulphur.....	4.13
Iron.....	28.50
Manganese.....	7.64
Silica.....	23.70
Alumina.....	4.00
Carbonic acid.....	4.31
Lime.....	7.30
Magnesia.....	0.33
Phosphorus.....	0.05

This was charged directly into a shaft furnace 1.8 meters long, 0.9 meter wide and 0.9 meter high. The melted material

ran out into a forehearth 1.2 meters long, 0.6 meter wide and 0.6 meter high. Two carbon electrodes, 30 centimeters square by 170 centimeters long, were used in the smelting chamber, and two electrodes, 25 centimeters square by 100 centimeters long, were put in the forehearth to reheat it for tapping.

The matte obtained analyzed:

	<i>Per Cent.</i>
Silica.....	0.80
Alumina.....	0.50
Iron.....	24.30
Manganese.....	1.40
Sulphur.....	22.96
Copper.....	47.90

The slag contained:

Silica.....	27.20
Alumina.....	5.20
Lime.....	9.90
Magnesia.....	0.39
Iron.....	32.50
Manganese.....	8.23
Sulphur.....	0.57
Phosphorus.....	0.06
Copper.....	0.10

The current used was 4,750 amperes at 119 volts; power factor = 0.9; 8,000 kilograms of ore mixture were smelted in 8 hours; consumption of electrodes 50 kilograms.

Required:

(1) A balance sheet of materials entering and leaving the furnace per hour.

(2) A balance sheet of the heat development and distribution in the furnace.

(3) The saving in cost of treatment per ton of ore, assuming electrodes to cost 4 cents per kilogram, coke \$20 per metric ton, and that when coke is used one-third of its calorific power leaves the furnace in the escaping hot gases. Assume all other costs similar, except that air blast costs \$0.10 per ton of ore smelted additional. Electric power \$6 per kilowatt-year.

(4) If the resulting slag were smelted electrically for ferro-

silicon, at an expenditure of 0.75 electric horse power-year per ton of ferro-silicon obtained, and other smelting costs were \$10 per ton, how much ferro-silicon would be obtained per ton of copper ore treated, and what would be its cost?

Solution:

(1) Balance sheet per 1,000 kg. of ore.

	<i>Charges</i>	<i>Matte</i>	<i>Slag</i>	<i>Gases</i>
Ore: 1,000 kg.				
Silica.....	237 kg.	1	236
Alumina.....	40 "	0.5	39.5
Iron.....	285 "	25	260
Manganese.....	76 "	1.5	74.5
Sulphur.....	41 "	24	5	12
Copper.....	51 "	50	1
Carbonic acid.....	43 "	43
Lime.....	73 "	73
Magnesia.....	3 "	3
Oxygen.....	137 "	2	74	61
Electrode:				
Carbon.....	6 "	6
		<hr/> 104	<hr/> 766	<hr/> 122

Composition of Slag.

	<i>Calculated.</i>	<i>Analyzed.</i>
Silica.....	29.5 per cent.	27.2 per cent.
Alumina.....	5.0 "	5.2 "
Lime.....	9.2 "	9.9 "
Iron.....	32.5 "	32.5 "
Manganese.....	9.3 "	8.2 "
Sulphur.....	0.6 "	0.6 "

Heat Development.

Electric energy per hour:

$$\begin{aligned}
 4,750 \times 119 \times 0.9 &= 509 \text{ kilowatt-hours.} \\
 509 \times 860 &= 437,750 \text{ Cal. per hour.}
 \end{aligned}$$

Oxidation of carbon:

$$\begin{aligned}
 6 \times 4,300 &= 25,800 \text{ " " " } \\
 &\underline{\hspace{1cm}} \\
 &463,550 \text{ " " " }
 \end{aligned}$$

Heat Distribution.

Heat in matte:

$$104 \times 270 = 28,080 \text{ Calories.}$$

Heat in slag:

$$796 \times 400 = 318,400 \quad "$$

$$\text{Heat in gases} = 30,000 \quad "$$

$$\text{Loss by radiation}$$

$$\text{and conduction} = 87,070 \quad "$$

$$463,550 \quad "$$

The radiation and conduction loss is 19 per cent of the total heat generated in the furnace—a satisfactory showing. The useful effect of the furnace is nearly 75 per cent, reckoning as usefully applied heat that contained as sensible heat in the melted matte and slag. Nearly 90 per cent of this usefully applied heat is contained in the slag.

(3) If coke were used instead of electric heat, enough coke would have to be used to furnish 433,550 Calories plus the heat in the gases. Since the latter is assumed to be one-third of its calorific power, the coke must have a calorific power of 650,325 Calories, which at 7,000 Calories per kilogram would require 93 kg. of coke per 1,000 of ore smelted. The costs of coke and blowing engine would therefore be

Coke,	$93 \times 0.02 = \$1.96$
Engine,	0.10
Sum	<hr/> \$2.06

The cost of electrodes and electric energy, which would replace coke and blowing engine, would be:

Electrodes,	$6 \text{ kg.} \times \$0.04 = \0.24
Power	$509 \text{ kw.} \times \frac{6.00}{8,760} = 0.35$
Sum,	<hr/> \$0.59
Saving,	\$1.47

(4) The resulting slag contains, according to the balance sheet, 260 kg. of iron, 74.5 kg. of manganese, and 236 kg. of silica equal to 126 kg. of silicon. It should produce, if com-

pletely reduced, 460 kg. of alloy (omitting the carbon it might contain) of the approximate composition:

Fe	260 kg. = 56 per cent.
Mn	74 kg. = 13 "
Si	126 kg. = 28 "
	<hr/>
	460 kg.

Cost of power $\$6.00 \times \frac{1}{4} = \4.50 per ton.

Other costs 10.00 "

Total costs per ton	<hr/>	\$14.50
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This cost is very low, because of the very low figure assumed for power cost. However, the whole calculation points to the possibility of great saving in some localities in smelting down copper ores by electrically applied heat, and the possibility of cheaply producing, at the same spot, valuable ferro-silicon as a by-product.

CHAPTER II.

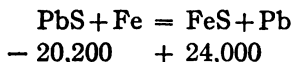
THE METALLURGY OF LEAD.

The extracting of lead from its ores and the refining of the crude metal to commercial lead, constitutes the metallurgy of lead. The chief ore is galena, lead sulphide, PbS ; but the carbonate, cerussite, PbCO_3 , and the sulphate, Anglesite, PbSO_4 , occur at some places in important quantities; the silicate, phosphate, molybdate, tungstate, chloride and native lead are rare minerals.

The reduction of the oxidized lead ores, such as often occur at the outcrops of sulphide veins, is very simple; carbon, the cheapest and most universal reducing agent, reduces them satisfactorily at a red heat, with some loss of lead by volatilization. The sulphide of lead, however, is not reducible by carbon; it requires other treatment. If we tabulate the most common sulphides according to their thermochemical heats of formation, expressed per unit weight of sulphur held in combination (32 kilograms), we find the common metals arranged as follows:

	<i>Calories.</i>
Potassium (K^2 , S).....	103,500
Calcium (Ca , S).....	94,300
Sodium (Na^2 , S).....	89,300
Manganese (Mn , S).....	45,600
Zinc (Zn , S).....	43,000
Cadmium (Cd , S).....	34,400
Iron (Fe , S).....	24,000
Cobalt (Co , S).....	21,900
Copper (Cu^2 , S).....	20,300
Lead (Pb , S).....	20,200
Nickel (Ni , S).....	19,500
Mercury (Hg , S).....	10,600
Hydrogen (H^2 , S).....	4,800
Silver (Ag^2 , S).....	3,000

A glance at this table shows us that some metals unite with sulphur more energetically than lead does, and others less energetically, and points to the theoretical possibility of decomposing lead sulphide by the agency of copper, cobalt, iron, cadmium, zinc, etc. Of these agents, iron is, of course, the cheapest and most available, and can be used to reduce lead sulphide with formation of iron sulphide.



Showing an excess heat development per 207 parts of lead set free, of $24,000 - 20,200 = 3,800$ Calories. If lead sulphide and iron are brought together at a red heat, at which heat the sulphide is molten, they react energetically with evolution of heat—enough theoretically to raise the temperature of the 207 kg. of lead and 88 kg. of iron sulphide some 280°C . The reaction is fairly complete if sufficient reducing agent is present and time is allowed, so that it can be used in assaying to determine lead by fire assay, but in commercial practice more or less undecomposed lead sulphide always remains in the iron sulphide, forming a sort of double sulphide or iron-lead matte.

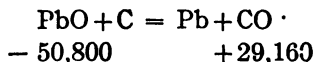
It is interesting to note, *en passant*, that lead vigorously reduces silver sulphide, the liberated silver alloying with the excess of lead. This reaction is accompanied by a large evolution of heat, as the table shows, is the basis of the ordinary assaying methods for silver ores, and is used commercially to extract silver from its ores wherever lead is plentiful.

The affinity of lead for oxygen is a no less interesting subject, since it concerns not only the reduction of oxide ores but also the roasting of sulphide ores to oxide, and very largely controls the refining of impurities from lead by methods involving oxidation. The heat of combination of some of the more common elements with oxygen, expressed per unit weight of 16 kilograms of oxygen held in combination, is as follows:

	Calories.
Magnesium (Mg, O).....	143,400
Calcium (Ca, O).....	131,500
Aluminium $\frac{1}{2}$ (Al^2 , O^2).....	130,870
Sodium (Na^2 , O).....	100,900
Silicon $\frac{1}{2}$ (Si , O^2).....	98,000

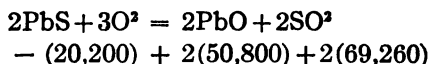
	<i>Calories.</i>
Manganese (Mn, O).....	90,900
Zinc (Zn, O).....	84,800
Tin $\frac{1}{2}$ (Sn, O ²).....	70,650
Iron (Fe, O).....	65,700
Iron $\frac{1}{3}$ (Fe ² , O ³).....	65,200
Nickel (Ni, O).....	61,500
Hydrogen (H ² , O).....	58,060
Antimony $\frac{1}{3}$ (Sb ² , O ³).....	55,630
Arsenic $\frac{1}{3}$ (As ² , O ³).....	52,130
Lead (Pb, O).....	50,800
Carbon $\frac{1}{2}$ (C, O ²).....	48,600
Bismuth $\frac{1}{3}$ (Bi ² , O ³).....	46,400
Copper (Cu ² , O).....	43,800
Sulphur $\frac{1}{2}$ (S, O ²).....	34,630
Sulphur $\frac{1}{3}$ (S, O ³).....	30,630
Carbon (C, O).....	29,160
Mercury (Hg, O).....	21,500
Silver (Ag ² , O).....	7,000

Reduction of Lead Oxide.—An inspection of above table shows that lead oxide is a weak oxide, weaker than the oxides of most of the common metals. It is reduced to metallic lead by many reagents with evolution of heat. It is also reduced by some weaker reagents with absorption of heat, provided that the oxide formed is gaseous and the necessary heat energy is supplied from outside. For instance,



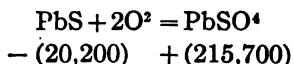
involves an absorption of 21,640 Calories, or several times as much heat as is necessary to raise the reacting substances, PbO and C, to the reacting temperature, a red heat. The reaction is endothermic, absorbing heat, and therefore only progresses *in measure* as the necessary calories are supplied from outside. The fact that all the substances concerned are liquid or solid except the product CO, gives a predisposing cause which facilitates the reaction, that is, the reaction can only go one way, since the CO gas escapes from the sphere of action as soon as formed.

Oxidation of Lead Sulphide.—When PbS is roasted, that is, heated to redness with free access of air, both the sulphur and the lead tend to oxidize, generating a large heat of oxidation, against which there is absorbed only the comparatively feeble heat of decomposition of PbS. The equation may be discussed as



The net heat evolved in the equation is $240,120 - 40,400 = 199,720$ Calories, which is 33,290 Calories per unit weight (16 kg.) of oxygen used, or 418 Calories for each kilogram of lead sulphide oxidized. This great heat of oxidation, evolved in roasting, is quite sufficient, in fact more than sufficient, to provide the heat required for self-roasting without the use of any other fuel, the chief difficulty is really to keep the charge from getting too hot and melting everything down to a liquid before the roasting is anywhere near complete. In the ordinary hand-worked reverberatory roaster, the oxidation is so slow that the fire on the grate really controls the temperature on the hearth, and the temperature of the roasting ore can be regulated accordingly. Where the roasting is done quickly, by an air blast, as in "Pot Roasting," the temperature is kept down somewhat by previously roasting off part of the sulphur, or by liberally wetting the charge, or by using limestone in with the ore, to absorb by its decomposition into CaO and CO² a large part of the excess heat—while the melting down of the charge is prevented by the mechanical interference presented by intermixed, inert and infusible material, such as silica, lime, etc., which simply prevents the really melted globules of sulphide from running together and thus melting down to a liquid mass.

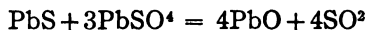
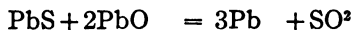
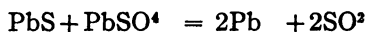
An interesting variation is the roasting of lead sulphide to sulphate; some of this always forms, due to the high formation heat and difficult decomposability of the sulphate.



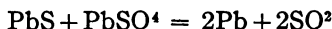
The net heat evolved is $215,700 - 20,200 = 195,500$ Calories, or 48,875 Calories per unit weight (16 kg.) of oxygen used, or 818 Calories for every kilogram of lead sulphide so oxidized.

This is a high heat of oxidation, and explains the great tendency to form sulphate observed during roasting. If the conditions could be found whereby only this reaction occurred, the sulphate roasting could be easily made automatic without outside fuel. There is needed, at the present time, a careful laboratory investigation of the conditions, mechanical, physical, chemical and thermal, for the roast exclusively to sulphate—just as a bit of badly needed metallurgical information.

Double Reactions.—A large part in the metallurgy of lead is played by double reactions, such as the following:

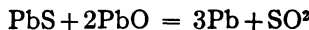


On roasting lead sulphide for a short time, either lead or lead sulphate or mixtures of these are formed, according to the temperature and excess of air provided. With large excess of air and low temperature, and especially in presence of infusible materials which act as catalyzers (*i.e.*, which promote the union of SO_2 with O, and consequent formation of SO_3 and PbSO_4), sulphate may be formed almost exclusively. If the temperature is then raised, the tendency of PbSO_4 to react upon the undecomposed PbS rapidly gets stronger, until at an orange heat this takes place rapidly and fairly completely, forming the one single gaseous product, SO_2 .



$$- (20,200) - (215,700) + 2(69,260)$$

Net deficit, 97,380 Calories.

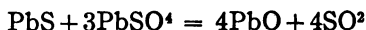


$$- (20,200) - 2(50,800) + (69,260)$$

Net deficit, 52,540 Calories.

In both these cases the well-known phenomena of an endothermic reaction are manifest—the high temperature and strong firing necessary, and the formation of a single gaseous product from non-gaseous materials, assisting the reaction.

The reaction:



$$- 20,200 - 3(215,700) + 4(50,800) + 4(69,260)$$

Net deficit, 187,060 Calories,

is supposed to take place in "pot roasting" where excess of air is blown through the finely divided material, but it is too endothermic a reaction to take place in a pot-roasting operation to more than a very subsidiary extent.

Oxidation Refining.—Impure lead is refined or "softened" by oxidation at a red heat. We must expect a great deal of lead to be oxidized in this operation, simply because of its preponderating mass, but the impurities present will oxidize relatively faster or slower than lead in proportion as their affinity for oxygen is relatively greater or less. The skimmings or slags obtained during softening are always principally composed of lead oxide, PbO , but they come off containing, in order, zinc, tin, antimony, arsenic, bismuth and small quantities of silver. During cupellation down to silver, which is continued oxidation until all the lead is oxidized, bismuth oxide is concentrated in the last parts of lead oxide formed, which may also carry silver in small amount; before this happens, however, the lithage formed is almost chemically pure.

The converse of these oxidation reactions also holds, viz.: differential reduction. Taking a softening skimming rich in antimony, for instance, it is possible by mixing it with a small amount of reducing agent, such as carbon, to reduce out of it all the silver and considerable of the lead which it contains without reducing much antimony. This leaves the remaining unreduced material desilverized and poorer in lead, or richer in antimony, and on subsequent reduction of this by excess of reducing agent a rich antimony-lead alloy is obtained. The easy reducibility of lead oxide is complementary to the slow oxidation of lead; both facts are clear from the heat of formation of the various metallic oxides, and both are extensively utilized in the metallurgy of lead.

THE VOLATILITY OF LEAD.

The melting point of lead is 326° , its mean specific heat in the solid state $0.02925 + 0.000019t$, heat in melted lead at its melting point 11.6 Calories, latent heat of fusion 4.0 Calories, heat in just melted lead 15.6 Calories, specific heat in the liquid state 0.042—and approximately constant—boiling point at normal atmospheric pressure about $1,800^{\circ}$ C., latent heat of vaporization, calculated by Trouton's rule (23 T) 47,680

Calories per molecular weight = 230 Calories per kilogram, assuming the vapor monatomic, specific gravity of vapor 103.5, referred to hydrogen gas at the same temperature and pressure, or, theoretically, 9.315 kg. per cubic meter at 0° C. and 760 mm. pressure, as a standard datum.

The question of the volatility of lead at other temperatures than 1,800° C. is highly important in the smelting of lead ores, yet is practically an unknown quantity. The following is an attempt to calculate these data, so important in practical metallurgy.

The vapor tension curve of mercury is known for very low and up to comparatively high pressures. A rule has been observed between mercury and water vapor, in that the absolute temperatures at which these two substances have the same vapor tensions are found to stand in the ratio 1.7 to 1 through a large range of temperatures. Since lead vapor is in all probability monatomic, like mercury vapor, we will deduce the vapor tension curve of lead from that of mercury, using the constant ratio derived from the two temperatures at which their respective vapors have atmospheric tension, viz.:

$$\frac{TPb}{THg} = \frac{1,800 + 273}{357 + 273} = \frac{2,073}{630} = 3.3$$

The following table gives the most reliable data for the vapor tension curve of mercury, and the corresponding data calculated for lead, assuming the constant ratio 3.3 between the absolute temperatures at which they have the same vapor tension:

<i>Tension of Vapor</i> <i>mm. of Hg.</i>	<i>Mercury</i> <i>C°</i>	<i>Lead</i> <i>C°</i>
0.0002	0	625
0.004	33	735
0.045	67	844
0.28	100	954
1.47	133	1,064
5.73	167	1,173
18.25	200	1,283
50.	233	1,393
106.	267	1,502

<i>Tension of Vapor</i> <i>mm. of Hg.</i>	<i>Mercury</i> C°	<i>Lead</i> C°
242.	300	1,612
484. <i>Atmospheres.</i>	333	1,722
760. = 1.0	357	1,800
849. = 1.1	367	1,841
1588. = 2.1	400	1,951
4.3	450	2,116
8.0	500	2,280
13.8	550	2,445
22.3	600	2,609
34.	650	2,774
50.	700	2,938
72.	750	3,103
102.	800	3,267
137.5	850	3,436
162.	880	3,525

From the above table a vapor pressure curve of mercury and lead can be constructed. An examination of the data shows that lead is certainly volatile to a minute extent at a low red heat, and that a current of inert gas passing across the surface of melted lead at that temperature certainly carries away vapor of lead; at the melting point of silver the tension is only about one-quarter of a millimeter, or one three thousandth of an atmosphere, yet this means that each cubic meter of inert gas carries off one three-thousandth of its volume, or one-thirtieth of 1 per cent of its volume, of lead vapor. At 1,300°, the temperature of a commercial zinc retort, or of a lead smelting furnace, the tension is about one-fortieth of an atmosphere, which would mean that any other gas or vapor could carry 2.5 per cent of its volume of lead vapor with it. It must be remembered, moreover, that such gas saturated with lead vapor if suddenly cooled does not deposit its excess of lead vapor as liquid lead, but that a suspension similar to hoarfrost almost inevitably results, the so-called "lead fume," which is simply molecularly divided liquid or solid lead carried in suspension by a current of gas. The lead vapor is thus almost entirely carried out of the furnace without condensation and deposition.

Looking at the higher pressures, we can understand why an

explosive reaction results when PbO is reduced by finely divided aluminium, the "aluminothermic" reaction. The immense heat liberated in the reaction,



220,000 Calories, raises the products to an electric furnace temperature, to some 3,000° C., at which temperature the lead vapor has a maximum tension, according to our table, of 60 atmospheres. No wonder, then, that when Tissier tried this test for the first time, in 1857, using a piece of sheet aluminium weighing less than 3 grams (0.1 ounce), "*le creuset a été brisé en mille pieces et les portes du fourneau projetées au loin*"—the crucible was broken into a thousand pieces and the doors of the furnace blown to a distance.

ROASTING OF LEAD ORES.

The principal operations in the metallurgy of lead are the roasting of the ore, its reduction to metal and the refining of the crude metal.

The chief ore of lead being galena, PbS, the operation of roasting it in air converts it partly into PbO and partly into PbSO₄. Since PbS is easily fusible, and is volatile *per se* at a yellow heat, it is necessary to roast carefully and slowly, avoiding high temperatures, which first make the ore sticky or pasty and afterwards fuse it, thus practically stopping the roasting reaction. The only manner in which rapid roasting can be done is by having the ore mixed with so much infusible inert matter, like lime, that the globules of melted sulphide cannot run together, but are kept isolated and continue to oxidize on their surfaces, the mass being meanwhile kept "open" or porous by the inert, infusible material, to allow the rapid passage of air through the mass. This is the principle of "pot roasting"—the most radical improvement of recent years in the metallurgy of lead.

Problem 123.

A Savelsberg "pot roaster" treats 5 tons of ore mixture, consisting of 100 parts lead ore, 10 parts quartzose silver ore, 10 parts spathic iron ore, 19 parts limestone. The lead ore is galena ore, containing 78 per cent of lead and 15 per cent of

sulphur; the silver ore may be called silica sand; the spathic iron ore FeCO_3 ; the limestone CaCO_3 . The mixture is moistened with 5 per cent of its weight of water. Air blast is kept constant at 7 cubic meters per minute, blower displacement at 15°C ., and the operation lasts 18 hours, leaving 2 per cent of sulphur in the product, which may be assumed as undecomposed PbS . Gases produced contain approximately 10 per cent of SO_2 and 5 per cent free oxygen; 50 kg. of charcoal is used to start the operation, and is assumed to be pure carbon.

Required:

- (1) The weight of product and its percentage composition.
- (2) The complete analysis of the gases escaping.
- (3) The efficiency of delivery of the blower.
- (4) The proportion of the heat generated by the oxidation of the ore which is absorbed in the decomposition of the limestone.
- (5) The proportion of the heat generated in the pot used in evaporating the moisture of the charge.
- (6) The proportion of the heat generated in the pot carried away by the gases at an average temperature of 300°C .
- (7) Make a heat balance sheet of the whole operation.

Solution:

- (1) The components of the 5-ton (= 5,000 kilos) charge are:
- | | | | | | |
|-----------------|----------|--------------------|----------|-----------------|---------|
| Galena..... | 3597 kg. | = Pb | 2806 kg. | S: | 540 kg. |
| Silver ore..... | 360 " | = SiO_2 : | 360 " | | |
| Iron ore..... | 360 " | = FeO : | 224 " | CO_2 : | 136 " |
| Limestone..... | 683 " | = CaO : | 382 " | CO_2 : | 301 " |

Approximate composition of product:

PbO.....	$2806 \times \frac{223}{207}$	= 3023 kg.
SiO_2		= 360 "
FeO		= 224 "
CaO		= 382 "
		<hr/>
		3989 "

But, since product contains 2 per cent of sulphur as undecomposed PbS , the above weight is only 99 per cent of the

weight of the roasted ore, because the lead combined with this sulphur has been calculated above to PbO, and the O in PbO is only half the weight of the S in PbS. The above weight is short, therefore, by an amount equal to one-half the weight of the sulphur present, and since the latter is 2 per cent of the roasted ore the above weight is 1 per cent short. The corrected weight of the roasted ore is, therefore,

$$3,989 \div 0.99 = 4,029 \text{ kg.},$$

and its sulphur content 81 kg., corresponding to 521 kg. of lead, or 602 kg. of PbS. This leaves present, as PbO, 2,806 - 521 = 2,285 kg. of lead, equal to $2,285 \times 223/207 = 2,461$ kg. of PbO.

Revised composition of product:

PbO.....	2461 kg.	= 61 per cent
PbS.....	602 "	= 15 "
SiO ²	360 "	= 9 "
FeO.....	224 "	= 5 "
CaO.....	382 "	= 9 "
	<hr/>	
	4029 "	(1)

(2) The charge gives to the gases

H ² O	$5000 \times 0.05 = 250$ kg.
CO ²	$(50 \times 3.67) + 136 + 301 = 620$ "
S	$540 - 81 = 459$ "

and the blast gives to the charge

$$\text{O } 2461 - 2285 = 176 \text{ kg.}$$

The volume of SO² produced from 459 kg. of sulphur, which makes 918 kg. of SO², will be, at standard conditions,

$$918 \div \left(0.09 \times \frac{64}{2}\right) = 319 \text{ cubic meters.}$$

The free oxygen in the gases is half the volume of the SO², and, therefore, will be exactly one-quarter of its weight.

The volumes of H²O and CO² present in the gases, at standard conditions, are

$$\text{H}^2\text{O} \quad 250 \div \left(0.09 \times \frac{18}{2}\right) = 309 \text{ cubic meters.}$$

$$\text{CO}^2 \quad 620 \div \left(0.09 \times \frac{44}{2}\right) = 313 \quad " \quad "$$

The nitrogen present is that in the air used, or 10/3 the weight of oxygen in the air. The latter is the weight of oxygen in the PbO of the roasted charge, plus the oxygen necessary to burn the 50 kg. of charcoal, plus the oxygen oxidizing sulphur to SO² and the free oxygen in the gases.

O in PbO.....		=	176 kg.
O to burn C.....	$50 \times \frac{32}{12}$	=	133 "
O to burn S.....	$459 \times \frac{32}{32}$	=	459 "
Free O ² in the gases.....		=	230 "
	Total		998 "
N ² corresponding.....		=	3327 "

Composition of escaping gases:

				<i>Per Cent.</i>
Nitrogen.....	3327 kg.	=	2609 cu. meters	= 70.3
Oxygen.....	230 "	=	159 " "	= 4.3
SO ²	918 "	=	319 " "	= 8.6
CO ²	620 "	=	313 " "	= 8.5
H ² O vapor.....	250 "	=	309 " "	= 8.4
	3709			100.

(2)

(3) Oxygen delivered by blast..... 998 kg.

Nitrogen in the blast..... 3327 "

Air delivered..... 4325 "

Volume at 0° = $4325 \div 1.293$ = 3345 cu. meters.

Volume at 15° = $3345 \times \frac{288}{273}$ = 3529 " "

Displacement of blower at 15°

$$7 \times 60 \times 18 = 7560 \quad " \quad "$$

$$\text{Efficiency of blower} \quad \frac{3529}{7560} = 0.467 = 46.7 \text{ per cent.} \quad (3)$$

(4) The heat generated in the oxidation of the ore consists of the heat of formation of the PbO formed, plus that of the SO², and less that of the PbS decomposed. This is not the complete heat balance of the whole operation, but simply that concerned with the oxidation of the galena.

Heat of oxidation of Pb to PbO

$$2285 \text{ kg. Pb.} \times 245 = + 559,825 \text{ Cal.}$$

Heat of oxidation of S to SO²

$$459 \text{ kg. S} \times 2164 = + 993,275 \quad "$$

Heat of formation of PbS decomposed

$$2285 \text{ kg. Pb} \times 98 = - 223,930 \quad "$$

$$\text{Roasting heat} = + 1,329,170 \quad "$$

The decomposition of the limestone, producing 301 kg. of CO², absorbs

$$301 \times 1,026 = 308,825 \text{ Cal.}$$

The proportion of the roasting heat thus absorbed is

$$\frac{308,825}{1,329,170} = 0.232 = \mathbf{23.2} \text{ per cent.} \quad (4)$$

(5) The 5-ton charge is moistened with 5 per cent of its weight of water, or 250 kgs., in order to keep down the temperature. This absorbs, simply in becoming vapor,

$$250 \times 606.5 = 151,625 \text{ Cal.,}$$

Which, on the heat generated in the roasting operation, is

$$\frac{151,625}{1,329,170} = 0.114 = \mathbf{11.4} \text{ per cent.} \quad (5)$$

(6) If the gases pass away at an average temperature of 300°, and the air comes in at an average temperature of 15°, the

gases cool off the pot to the extent of the difference between these two heat capacities:

Heat in the air entering:

$$3345 \text{ m}^3 \times [0.303 + 0.000027(15)] \times 15 = 15,225 \text{ Cal.}$$

Heat in gases escaping:

$$\begin{array}{lcl} \text{N}^2 & 2609 \text{ m}^3 \} & \times [0.303 + 0.000027(300)] = 861.1 \text{ Cal. per } 1^\circ. \\ \text{O}^2 & 159 \text{ m}^3 \} & \\ \text{SO}^2 & 319 \text{ m}^3 & \times [0.36 + 0.0003(300)] = 143.6 \text{ " } \\ \text{CO}^2 & 313 \text{ m}^3 & \times [0.37 + 0.00022(300)] = 136.5 \text{ " } \\ \text{H}^2\text{O} & 309 \text{ m}^3 & \times [0.34 + 0.00015(300)] = 119.0 \text{ " } \\ & & \hline & & 1260.2 \text{ " } \end{array}$$

$$\text{Total} = 1260.2 \times 300 = 378,060 \text{ Cal.}$$

Proportion of the total roasting heat thus carried out:

$$\frac{362,835}{1,329,070} = 0.280 = \mathbf{28.0} \text{ per cent.} \quad (6)$$

(7)	<i>Heat Available.</i>	<i>Calories.</i>
Sensible heat of air blast, at 15°.....		15,225
Combustion of charcoal.....		405,000
Net heat generated by the roasting.....		1,329,170
		<hr/>
Total.....		1,749,395

Heat Distribution.

Sensible heat in the hot gases..... 378,060 = 22 per cent.

Decomposition of carbonates:

Calcium carbonate.....	308,825 = 18	"
Iron carbonate.....	76,980 = 4	"
Evaporation of moisture.....	151,625 = 9	"
Sensible heat of product, at 400°....	400,000 = 23	"
Loss by radiation and conduction...	433,905 = 25	"

$$\hline 1,749,395$$

REDUCTION OF ROASTED ORE.

If the roasted ore is reduced in reverberatory furnaces, the chances are that the undecomposed sulphide it contains will react with the oxide or sulphate, forming metal and SO^2 , and

thus eliminating almost all of the sulphur left in the roasted ore; this results in the formation of no matte, or at most of very little rich matte. If the roasted ore is reduced in shaft furnaces, the carbonaceous fuel and strong reducing atmosphere of the same, tend to reduce oxides to metal and sulphates to sulphides before they reach the temperature at which they can react on sulphide, thus cutting out very largely the double reaction, and throwing into matte the larger part of the sulphur left in the roasted ore. This is highly advantageous if the ore has copper in it, even if only in small amount, as the matte will concentrate the copper in it, is easily separated from the metal and the slag, and forms a valuable by-product. Since most lead ores contain some copper, enough to make it pay to save it, the roasting of these is never pushed to completion, and the reduction in low shaft furnaces, run at moderate temperature, is pursued with the object of producing a copper-iron matte. Any arsenic or antimony left in the roasted ore is likely also to form *spiess*, a compound of arsenic and antimony with iron, copper, nickel, cobalt, lead and silver, which is heavier than matte, but lighter than lead, and separates out in the cooling pots between these. It is a highly undesirable product, because of its complexity and the difficulty of satisfactorily and cheaply separating its constituents; it is always to be advised to remove arsenic and antimony as completely as possible in the roasting operation, even at the expense of removing too much sulphur, and then to supply the sulphur needed in the smelting operation by mixing with the dead-roasted ore some raw sulphide ore free from arsenic and antimony, if such can be obtained.

In calculating the charge for such a smelting operation, the roasted ore must be charged with such amounts of iron ore and limestone as will, together with the gangue of the ore and the ash of the fuel used, make an easily fusible slag. To produce such a slag is of fundamental importance, since it must melt and become thinly liquid at the moderate temperature necessarily prevailing in a lead furnace. Experience has shown that a typical lead slag will contain about 30 per cent SiO_2 , 40 per cent FeO and 20 per cent CaO , with 10 per cent allowed for other ingredients, such as Al_2O_3 , etc., or in more general terms, that SiO_2 , FeO and CaO are best present in the propor-

tions 30 : 40 : 20. The other limitations are that a certain amount of hand-picked slag is always returned to the furnace for re-smelting and purification from matte, and that the fuel, coke, cannot melt more than a certain amount, say seven times its weight of inert material. With these conditions in mind, we will work out a typical smelting problem, the data for which are taken from Hofman's *Metallurgy of Lead*.

Problem 124.

A mixture of lead carbonate ore and galena (which represents pretty closely a partially roasted sulphide ore) is smelted with the addition of iron ore and limestone. The charges for the furnace consist of 1,000 pounds of burden (material to be smelted) and 150 pounds of coke (containing 10 per cent ash), and the 1,000 pounds consist of 100 pounds return slags and 900 pounds of lead ore, iron ore and limestone. The percentage composition of these materials is:

	<i>Lead Ore.</i>	<i>Iron Ore.</i>	<i>Limestone.</i>	<i>Ash of Coke.</i>
SiO ²	32.6	4.3	2.7	40.3
FeO.....	14.8	72.4	4.5	26.5
MnO.....	4.3	1.7
CaO.....	2.2	3.1	37.3	6.9
MgO.....	5.3	11.9	2.4
Al ² O ³	2.5	20.4
BaO.....	1.5			
ZnO.....	2.4	The iron present in these materials is really present mostly as Fe ² O ³ and only partly as FeO, but the analysis is expressed usually as FeO in order to facilitate the slag calculations. The analyses, as given, are not expected to add up to 100.		
S.....	4.4			
As.....	0.5			
Pb.....	20.7			
Cu.....	2.9			
Ag.....	0.17			
	54.4			

In making the calculations, assume that the slag to be produced contains SiO²: FeO: CaO in the ratio 30 : 40 : 20; that the FeO here expressed includes the MnO, calculated to its FeO equivalent, and the CaO includes the MgO, BaO, and ZnO calculated to their CaO equivalent. Assume also that all the ZnO of the charge goes into the slag, all the sulphur into matte, all the arsenic into speiss, of the formula Fe⁵As, all the silver and lead into the lead bullion.

Requirements:

- (1) The proportions of lead ore, iron ore and limestone to be used in the 900 pounds of these to a charge.
- (2) The weight and composition of the slag formed.
- (3) The weight and composition of matte formed.
- (4) The weight and composition of speiss formed.
- (5) The weight and composition of lead bullion formed.
- (6) A balance sheet of the essential materials entering and leaving the furnace.

Solution:

(1) There are really only two unknown weights to be determined, for the sum of the three weights required is to be 900. Similarly, the ratio 30 : 40 : 20 really gives two conditions to be fulfilled, since there are practically two ratios to be worked to. The simplest method of solution is, undoubtedly, the algebraic one, letting x and y represent two of the ores, $900 - (x + y)$ the other, and then working out the weights of SiO_2 , FeO and CaO in the slag, expressed in terms of x and y . The ratio 30 : 40 : 20 then gives us two independent equations, containing the two unknowns, and the problem is solved.

Let x = weight of lead ore.

y = weight of iron ore.

$900 - x - y$ = weight of limestone.

15 = weight of ash of coke.

100 = weight of return slags.

Calculation of FeO going into Slag.

Sulphur in 100 parts ore	4.4 lbs.
Copper in 100 parts ore	2.9 "
Sulphur united with Cu to form Cu_2S	0.7 "
Sulphur left over to form FeS	3.7 "
Iron needed to form $\text{FeS} = 3.7 \times \frac{56}{32}$	= 6.5 "
FeO corresponding to this Fe = $6.5 \times \frac{72}{56}$	= 8.4 "
Arsenic in 100 parts of ore	0.5 "
Iron required to form $\text{Fe}_5\text{As} = 0.5 \times \frac{280}{75}$	= 1.9 "

$$\text{FeO corresponding to this Fe} = 1.9 \times \frac{72}{56} = 2.4 \text{ lbs.}$$

$$\text{Total FeO disappearing in matte and speiss} = 10.8 \text{ "}$$

$$\text{FeO left over to go into slag} = 14.8 - 10.8 = 4.0 \text{ "}$$

Therefore x parts of lead ore contributes to the slag:

$$\begin{aligned} \text{SiO}_2 & \dots\dots\dots 0.326 x \\ \text{FeO} & \dots\dots\dots 0.040 x \\ \text{MnO} & \dots\dots\dots 0.043 x = 0.044 x \text{ FeO.} \\ \text{CaO} & \dots\dots\dots 0.022 x \\ \text{MgO} & \dots\dots\dots 0.053 x = 0.074 x \text{ CaO.} \\ \text{Al}_2\text{O}_3 & \dots\dots\dots 0.025 x \\ \text{BaO} & \dots\dots\dots 0.015 x = 0.006 x \text{ CaO.} \\ \text{ZnO} & \dots\dots\dots 0.024 x = 0.017 x \text{ CaO.} \end{aligned}$$

The FeO equivalent of MnO is 72/71 the MnO; the CaO equivalent of MgO is 56/40 the MgO, of BaO is 56/141 the BaO, of ZnO is 56/81 the ZnO. These ratios are the chemically equivalent values of these oxides, as taken from their molecular weights. Adding all these together, our lead ore contributes to the slag the equivalent of

$$\text{SiO}_2 \text{ } 0.326 x, \text{ FeO } 0.084 x, \text{ CaO } 0.119 x.$$

The y parts of iron ore similarly contributes to the slag:

$$\text{SiO}_2 \text{ } 0.043 y, \text{ FeO } 0.741 y, \text{ CaO } 0.031 y.$$

The $900 - x - y$ parts of limestone contributes likewise:

$$\begin{aligned} \text{SiO}_2 & \text{ } 0.027(900 - x - y) \\ \text{FeO} & \text{ } 0.045(900 - x - y) \\ \text{CaO} & \text{ } 0.373(900 - x - y) \\ \text{MgO} & \text{ } 0.119(900 - x - y) = 0.167(900 - x - y) \text{ of CaO.} \end{aligned}$$

Therefore, total contribution of the limestone to the slag:

$$\begin{aligned} \text{SiO}_2 & \text{ } 0.027(900 - x - y), \text{ FeO } 0.045(900 - x - y), \\ & \text{CaO } 0.540(900 - x - y). \end{aligned}$$

Contribution of ash of fuel to the slag, in similar manner:

$$\text{SiO}_2 \text{ } 6.1 \qquad \text{FeO } 4.0 \qquad \text{CaO } 1.4$$

Adding all these together, we have in the slag:

$$\begin{array}{l} \text{SiO}_2 \dots\dots\dots 30.4 + 0.299 x + 0.016 y \\ \text{FeO} \dots\dots\dots 44.5 + 0.039 x + 0.696 y \\ \text{CaO} \dots\dots\dots 487.6 - 0.421 x - 0.509 y \end{array}$$

According to assumption, these ingredients as thus summated should bear the relations 30 : 40 : 20. We therefore have

$$30.4 + 0.299 x + 0.016 y = \frac{30}{20} (487.6 - 0.421 x - 0.509 y)$$

$$44.5 + 0.039 x + 0.696 y = \frac{40}{20} (487.6 - 0.421 x - 0.509 y)$$

$$\begin{array}{lll} \text{Whence} & x = \text{lead ore} & = 523 \text{ lbs.} \\ & y = \text{iron ore} & = 274 \text{ "} \\ & 900 - x - y = \text{limestone} & = 103 \text{ "} \end{array} \quad (1)$$

(2) With the weights of materials used, as calculated, we can calculate the weights of the ingredients of the slag as:

	Lead Ore.	Iron Ore.	Limestone.	Coke Ash.	Total.
SiO ₂	170.5	11.8	2.8	6.1	191.2
FeO.....	20.9	198.4	4.6	4.0	227.9
MnO.....	22.5	4.7	27.2
CaO.....	11.5	8.5	38.4	1.0	59.4
MgO.....	27.7	12.3	0.4	40.4
Al ₂ O ₃	13.1	3.1	16.2
BaO.....	7.8	7.8
ZnO.....	12.6	12.6
					<hr/> 582.7

Percentage Composition and Check on Ratio.

SiO ₂	32.8 per cent			
FeO.....	39.0	"		
MnO.....	4.7	"	= 4.8 per cent FeO.	
CaO.....	10.2	"		
MgO.....	6.9	"	= 9.7	" CaO.
Al ₂ O ₃	2.8	"		
BaO.....	1.3	"	= 0.5	" CaO.
ZnO.....	2.2	"	= 1.5	" CaO.

$$\begin{array}{l} \text{Summated SiO}_2 : \text{FeO} : \text{CaO} \\ = 32.8 : 43.8 : 21.9 = 30 : 40 : 20 \end{array}$$

(3) Sulphur in 523 lbs. of lead ore	= 23.0 lbs.
Copper in 523 lbs. of lead ore	= 15.2 "
Sulphur to form Cu_2S with this Cu	= 3.8 "
Sulphur to form FeS = 23.0 - 3.8	= 19.2 "
Fe to form FeS = $19.2 \times \frac{56}{32}$	= 33.6 "
FeS in matte = 19.2 + 33.6	= 52.8 "
Cu_2S in matte = 15.2 + 3.8	= 19.0 "
Total weight of matte	= <u>71.8</u> "

(3)

Composition of matte

Cu_2S = 26.5 per cent = Cu	= 21 per cent.
FeS = 73.5 " Fe	= 47 "
S	= 22 "

(3)

(4) Arsenic in 523 lbs. of lead ore	= 2.6 "
-------------------------------------	---------

Fe to form Fe^5As = $2.6 \times \frac{280}{75}$	= 9.7 "
---	---------

Weight of speiss formed	= <u>12.3</u> "
-------------------------	-----------------

(4)

Composition:	Fe 79 per cent
	As 21 "

(4)

(5) Lead in 523 lbs. of lead ore	= 108.3 lbs.
Silver in 523 lbs. of lead ore	= 0.9 "

109.2 "

(5)

Composition:	Pb 99.2 per cent.
	Ag 0.8 "

(5)

(6) Balance sheet of materials entering and leaving per 1,000 lbs. of burden:

<i>Charges.</i>		<i>Bullion.</i>	<i>Matte.</i>	<i>Speiss.</i>	<i>Slag.</i>	<i>Gases.</i>
Lead Ore 523						
SiO_2	170.5	170.5
FeO	77.4	...	Fe 33.6	Fe 9.7	Fe O 20.9	O 13.2
MnO	22.5	22.5
CaO	11.5	11.5

<i>Charges.</i>		<i>Bullion.</i>	<i>Matte.</i>	<i>Speiss.</i>	<i>Slag.</i>	<i>Gases.</i>
MgO	27.7	27.7
Al ₂ O ₃	13.1	13.1
BaO	7.8	7.8
ZnO	12.6	12.6
S	23.0	...	23.0
As	2.6	2.6
Pb	108.3	108.3
Cu	15.2	...	15.2
Ag	0.9	0.9
Iron Ore	274					
SiO ₂	11.8	11.8
FeO	198.4	198.4
MnO	4.7	4.7
CaO	8.5	8.5
Limestone	103					
SiO ₂	2.8	2.8
FeO	4.6	4.6
CaO	38.4	38.4
MgO	12.3	12.3
Ash of Fuel	15					
SiO ₂	6.1	6.1
FeO	4.0	4.0
CaO	1.0	1.0
MgO	0.4	0.4
Al ₂ O ₃	3.1	3.1
Return Slag	100	100.0
		<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
		109.2	71.8	12.3	682.7	13.2

THE ELECTROMETALLURGY OF LEAD.

As far as the present, the use of electrical methods in the metallurgy of lead has been confined to the Salom process of cathodic reduction of galena and the Betts process of refining crude lead bullion. Electrothermic methods of smelting, and even of roasting, are among future possibilities, as are also the leaching by suitable solvents and electrical precipitation of lead from the solutions, but they have not been commercially practiced.

The Salom process puts the powdered galena on a "hard-

lead " plate, in a solution of dilute sulphuric acid, and using a " hard-lead " anode, passes a strong current through, reducing PbS *in situ* to Pb with formation of H₂S (with some hydrogen) at the cathode and oxygen at the anode. It was run commercially on a fair scale at Niagara Falls. For further details reference may be made to *Transactions American Electrochemical Society*, Vol. I, p. 87; II, p. 65; IV, p. 101.

The Betts process consists in using impure lead as anode in a solution of lead fluo-silicate, PbF₂. SiF₄, strongly acid with HF. The refining plant and its operation are quite similar to a copper refining plant. The cathodes are sheet steel, greased, and the dense sheet lead deposited is stripped off from time to time.

Problem 125.

In a Salom apparatus powdered galena, density of powder 3.5, is placed in a layer 0.5 mm. thick on a revolving lead table having an effective treatment area of 2.25 square meters. Current density 330 amps. per square meter of cathode surface. Time of treatment of the layer 90 minutes. Electrolyte dilute H₂SO₄. Resistance of cell 0.001 ohm. Heats of formation: (Pb, S) 20,300; (H₂, S) 4,800 (as gas); (H₂, O) 69,000. Assume reduction to Pb complete.

Required:

(1) The efficiency of application of the amperes passing to the reduction of the galena, and the percentage of ampere efficiency lost by the evolution of hydrogen.

(2) The average composition of the gases coming from the cell and their volume per hour, at normal pressure and 20° C., assuming the electrolyte saturated with H₂S, H₂ and O₂ at starting.

(3) The working voltage absorbed, if the efficiency of reduction of galena were 100 per cent.

(4) The working voltage if the cell were kept running after all the galena was reduced.

(5) The average working voltage of the cell in actual operation and the distribution of this.

(6) The proportion of the power required by the cell which could be generated by burning the gases produced in a gas engine (if such were possible) at a thermo-mechanical efficiency of 100 per cent.

$$(1) \text{ Current used } 2.25 \times 330 = 742 \text{ amperes.}$$

Lead theoretically reducible in 90 minutes

$$0.00001035 \times 103.5 \times 60 \times 90 \times 742.5 = 4295 \text{ grams.}$$

Galena in the apparatus:

$$2.25 \times 10,000 \times 0.05 \times 3.5 = 3938 \text{ "}$$

Lead under treatment:

$$3938 \times \frac{207}{239} = 3410 \text{ "}$$

Ampere efficiency of the treatment:

$$\frac{3410}{4295} = 0.794 = 79.4 \text{ per cent.}$$

$$\text{Per cent of amperes evolving hydrogen} = 20.6 \text{ " (1)}$$

(2) If all the current evolved H^2S , the gases evolved would be:

$$\begin{array}{cc} 2H^2S & O^2 \\ 2 \text{ parts} & 1 \text{ part.} \end{array}$$

If all the current evolved H^2 , the gases would be:

$$\begin{array}{cc} 2H^2 & O^2 \\ 2 \text{ parts} & 1 \text{ part.} \end{array}$$

If 79.4 per cent of the current evolves H^2S and 20.6 per cent hydrogen, the average gases evolved will be:

$$\begin{array}{llll} H^2S & 1.588 \text{ parts} & = & 52.93 \text{ per cent.} \\ H^2 & 0.412 \text{ "} & = & 13.73 \text{ "} \\ O^2 & 1.000 \text{ "} & = & 33.33 \text{ "} \end{array} \quad (2)$$

The volume evolved per hour is found as follows:

Oxygen produced by 1 ampere hour

$$0.00001035 \times 8 \times 60 \times 60 = 0.29808 \text{ grams.}$$

Produced by 742.5 amperes, in one hour

$$0.29808 \times 742.5 = 221.3 \text{ "}$$

Volume at 760 mm. and 0° C.

$$221.3 \div 1.44 = 153.7 \text{ litres.}$$

Volume of gases produced per hour

$$153.7 \times 3 = 461. \text{ "}$$

$$= 0.461 \text{ cubic meter}$$

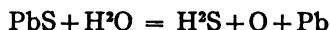
Volume at 20°

$$0.461 \times \frac{273 + 20}{273} = 0.495 \text{ " (2)}$$

(3) Voltage for ohmic resistance

$$0.001 \times 742 = 0.742 \text{ volts.}$$

Chemical work done if only H^2S is formed, per formula



$$\begin{array}{rcl} -20,300 & -69,000 & +4,800 = -84,500 \text{ Cal.} \end{array}$$

Per chemical equivalent concerned $= -42,250$ "

Voltage absorbed in chemical work

$$42,250 \div 23,040 = 1.83 \text{ volts}$$

Total voltage drop in the cell $1.83 + 0.74 = 2.59$ " (3)

(4) Chemical work done if only H^2 is liberated $= 69,000$ Cal.

Voltage absorbed in chemical work

$$\frac{69,000}{2} \div 23,040 = 1.49 \text{ volts.}$$

Total voltage drop in the cell $= 2.23$ (4)

(5) Voltage absorbed in chemical work if 79.4 per cent of the current evolves H^2S and 20.6 per cent H^2 :

$$(1.83 \times 0.794) + (1.49 \times 0.206) = 1.76 \text{ volts.}$$

Total voltage drop, in average running $= 2.50$ " (5)

Logically, the 1.76 volts absorbed in chemical decomposition in average running is properly calculated thus, from the energy evolved:

$$\frac{(42,250 \times 0.794) + (34,500 \times 0.206)}{23,040} = 1.76$$

(6) Heat of combustion of $\frac{1}{2}$ cubic meter of the average gas:

$$\text{H}^2\text{S} \quad 0.5293 \text{ m}^3 \times 5,513 = 2918 \text{ Cal.}$$

$$\text{H}^2 \quad 0.1373 \text{ m}^3 \times 2,614 = 359 \text{ "}$$

$$\text{Sum} = 3277 \text{ "}$$

Calorific power of gas produced per hour:

$$3277 \times 0.461 = 1511 \text{ Calories.}$$

Watt hours producible from this at 100 per cent thermo-mechanical efficiency:

$$1511 \div 0.860 = 1757 \text{ watts.}$$

Current used by the cell, average running:

$$742.5 \times 2.50 = 1856 \text{ watts.}$$

Proportion theoretically regainable:

$$\frac{1757}{1856} = 0.95 = 95 \text{ per cent.} \quad (6)$$

The reason why more power is theoretically regainable than is used in doing chemical work in the cell, is that the gas engine burns the sulphur of the PbS ultimately to SO_2 , and this is the source of great energy, while only a relatively small amount of energy was necessary to convert the PbS into H_2S ready for combustion.

Problem 126.

Lead bullion refined by the Betts process is 96.73 per cent lead, and the refined lead is practically pure. The anodes are 1.5 inches thick, and weigh, with lugs for suspension, 275 pounds. They are left in the tanks an average of nine days, running with 135 amps. per plate, whose active surface is 1,700 square inches. Space between anode and cathode $1\frac{1}{8}$ inches, specific resistance of solution 10 ohms. Each tank has twenty-two anodes and twenty-three cathodes, and produces an average of 545 pounds of lead per day. Power costs \$50 per electric horsepower-year, as delivered to the tanks. Drop per tank, due to resistance of contacts, 0.15 volt; specific gravity of pure lead, 11.35.

Required:

- (1) The weight of lead theoretically deposited by the current per day.
- (2) The ampere efficiency of the deposition.
- (3) The voltage drop per tank.
- (4) The amount of anode scrap to be remelted in percent of the total anode weight.
- (5) The average thickness of the cathode deposit per day.
- (6) The power costs per ton of impure lead refined.

Solution:

- (1) Lead theoretically deposited by 1 ampere per day

$$0.00001035 \times 103.5 \times 60 \times 60 \times 24 = 92.55 \text{ grams.}$$

Per anode per day, dissolved

$$\begin{aligned} 92.55 \times 135 \div 1000 &= 12.5 \text{ kg.} \\ &= 27.5 \text{ lbs.} \end{aligned}$$

Per tank, per day, deposited

$$27.5 \times 22 = 605 \quad (1)$$

(2) Efficiency of deposition

$$\frac{545}{605} = 0.90 = 90 \text{ per cent.} \quad (2)$$

(3) Amperes used per plate = 135

Current density per square inch

$$= 135 \div 1700 = 0.0794 \text{ amperes}$$

Current density per square centimeter

$$= 0.0794 \div 6.25 = 0.0127 \quad "$$

Distance of plates apart

$$= 1.17 \text{ inches}$$

$$= 2.93 \text{ cm.}$$

Resistance of 1 cm. cube of electrolyte

$$= 10 \text{ ohms.}$$

Voltage drop in electrolyte

$$10 \times 2.93 \times 0.0127 = 0.37 \text{ volt.}$$

Voltage drop in connections

$$= 0.15 \quad "$$

Total voltage drop per tank

$$= 0.52 \quad " \quad (3)$$

(4) Dissolved from anode in 9 days

$$545 \div 22 \times 9 = 223 \text{ lbs.}$$

Anode corroded in 9 days, assuming slime to fall off it

$$223 \div 0.9673 = 231 \text{ lbs.}$$

Anode scrap = 275 - 231

$$= 44 \quad "$$

Percentage of anode scrap

$$\frac{44}{275} = 0.16 = 16 \text{ per cent.} \quad (4)$$

(5) Deposit of lead one side of a cathode, per day

$$545 \div 44 = 12.4 \text{ lbs.}$$

$$= 5.636 \text{ kg.}$$

Area of 1 side of a cathode

$$= 850 \text{ sq. inches.}$$

$$= 5312 \text{ sq. cm.}$$

Deposit, per day, per sq. cm.

$$5636 \div 5312 = 1.06 \text{ grams.}$$

Volume of this deposit $1.06 \div 11.35 = 0.093$ cu. cm.

Therefore thickness deposited per day $= 0.93$ mm. (5)

(6) Bullion refined, per tank, per day

$$545 \div 0.9673 = 563 \text{ lbs.}$$

Power required per tank $2970 \times 0.52 = 1544$ watts.

$$= 2.06 \text{ e.h.p.}$$

Cost of power per year $= 50 \times 2.06 = 103.$ dollars.

per day $= 103 \div 365 = 0.28$ "

per ton of lead treated $0.28 \times \frac{2000}{563} = 0.99$ " (6)

CHAPTER III.

THE METALLURGY OF SILVER AND GOLD.

The processes most used for the extraction of silver and gold from their ores are the smelting of the ores with copper ores to matte and eventually blister copper, followed by electrolytic refining of the latter, or smelting with lead ores, followed by desilverization of the resulting lead bullion, cupellation of the rich lead, or electrolytic refining of the same. In all of these cases the silver or gold is a comparatively minute constituent of the ore, intermediate products and final metal, so that the metallurgy of silver or gold, after these methods, up to the production of impure silver or gold, or silver or gold bullion, is practically the metallurgy of copper or lead—both of which subjects we have considered at length.

When we obtain products in which the silver or gold is the chief constituent, we approach a condition in which calculations upon the precious metal contained may be based, but here again there are not the same conditions of economy so prominent in the metallurgy of lead or copper. It does not matter greatly, for instance, whether we use 50 cents' worth of one fuel or a dollar's worth of another in melting 1,000 ounces of silver worth over \$500; the question of which fuel is the cleanest or most convenient is of greater importance than the cost of the fuel.

The object of this introduction is to show that, until it comes to handling nearly pure silver or gold, close calculations as to amounts of reagents, running of furnaces, etc., are not practicable for silver or gold, *per se*.

ELECTROLYTIC REFINING OF SILVER BULLION.

The parting of gold and silver by acids is rapidly giving place to the cleaner and less expensive electrolytic separation. The bullion may be of quite variable composition. The following analyses of two samples give an idea of this variation.

	<i>Cupelled Silver.</i>	<i>Impure Silver.</i>
Ag.....	98.69	74.08
Pb.....	1.09	3.71
Cu.....	0.12	20.23
Fe.....	0.09	1.01
Au.....	0.0023	0.05

The electrolytic refining proceeds easiest with the nearly pure silver, because the impurities going into solution accumulate much more slowly, and the solution therefore requires purifying less frequently. On the other hand, the solution of a large amount of copper, iron or lead adds electromotive force to the circuit, since silver only is deposited, and thus decreases the electrical work to be done.

Problem 127.

Two varieties of silver bullion are refined electrolytically carrying

	<i>No. 1.</i>	<i>No. 2.</i>
Ag.....	98.69	74.08
Pb.....	1.09	3.71
Cu.....	0.12	20.23
Fe.....	0.09	1.01
Au.....	0.01	0.05

The slimes from each carry in percentages:

	<i>No. 1.</i>	<i>No. 2.</i>
Ag.....	60	55
Pb.....	10	5
Cu.....	5	15
Fe.....	3	5
Au.....	22	20

In each case all the gold goes into the slimes. A current density of 200 amperes per square meter of electrode surface is used, and the plates are 2 centimeters thick. Specific gravity of No. 1, 10.15; of No. 2, 9.79. There is anode scrap equal to 12 per cent of the weight of the plates. The working space between the electrodes is 4 cm. total current 220 amperes per tank, specific resistance of electrolyte 20 ohms. Deposited silver, 19.85 kg. per tank per day.

Required:

- (1) The ampere efficiency of the deposition of silver.
- (2) The weight of anode corroded in a tank per day.
- (3) The deficit in weight of silver in the electrolyte in each tank per day.
- (4) The electromotive force contributed to the circuit by the solution of impurities in the case of each bullion.
- (5) The total drop of potential across each tank, adding 10 per cent for loss in contacts.
- (6) The horse power-hours required per kilogram of silver deposited in each case.

Solution:

- (1) Silver deposited theoretically by one ampere, per day
 $0.00001035 \times 108 \times 60 \times 60 \times 24 = 96.58 \text{ grms.}$
 220 amperes deposit $96.58 \times 220 = 21,248 \text{ "}$
 $= 21.248 \text{ kg.}$

$$\text{Ampere efficiency } \frac{19.85}{21.248} = 0.934 = 93.4 \text{ per cent.} \quad (1)$$

This means that 6.6 per cent of all the silver which the current is capable of depositing is prevented from depositing by the nitric acid present, forming AgNO_3 . The electrolyte is silver nitrate with copper nitrate, and contains always about 1 per cent of free nitric acid, which thus acts chemically upon the deposited silver (or acts to prevent its deposition to this extent, whichever way we wish to look at it).

- (2) The weight dissolved, per 100 grams of anode corroded, is, assuming all the gold to appear in the slimes:

No. 1.

	<i>Anode.</i>	<i>Slimes.</i>	<i>Dissolved.</i>
Ag.....	98.69	0.03	98.66
Pb.....	1.09	1.09
Cu.....	0.12	0.12
Fe.....	0.09	0.09
Au.....	0.01	0.01

No. 2.

	<i>Anode.</i>	<i>Slimes.</i>	<i>Dissolved.</i>
Ag.....	74.08	0.14	77.94
Pb.....	3.71	0.01	3.70

	<i>Anode.</i>	<i>Slimes.</i>	<i>Dissolved.</i>
Cu.....	20.23	0.04	20.19
Fe.....	1.01	0.01	1.00
Au.....	0.05	0.05

The amount of current necessary to dissolve these weights will be the sum of the current which would be necessary to dissolve each constituent separately. These will be found in ampere-hours by dividing each by its electrochemical chemical equivalent $\times 3,600$.

No. 1.

	<i>Ampere-Hours.</i>
Ag..... $98.66 \div 0.001118 \times 60 \times 60$	= 24.51
Pb..... $1.09 \div 0.00107 \times 60 \times 60$	= 0.28
Cu..... $0.12 \div 0.00033 \times 60 \times 60$	= 0.12
Fe..... $0.09 \div 0.00029 \times 60 \times 60$	= 0.09
	<hr/>
	25.00

No. 2.

Ag..... $77.94 \div 4.025$	= 19.36
Pb..... $3.70 \div 3.856$	= 0.96
Cu..... $20.19 \div 1.185$	= 17.04
Fe..... $1.00 \div 1.044$	= 0.96
	<hr/>
	38.32

Since there is disposable $220 \times 24 = 5,280$ ampere-hours in a tank per day, there will be corroded the following weights of anodes per day in tanks containing Nos. 1 and 2, respectively;

$$\text{No. 1.....} \quad 100 \times \frac{5,280}{25} = \mathbf{21,120} \text{ Grams.}$$

$$\text{No. 2} \quad 100 \times \frac{5,280}{38.32} = \mathbf{13,779} \quad "$$

(3) There are dissolved in a tank, per day, the following weights of silver:

No. 1 anodes: $21,120 \times 0.9866$	= 20,837 Grams
No. 2 anodes: $13,779 \times 0.7794$	= 10,739 "
Deposit in each tank	= 19,850 "
Surplus in No. 1 tank	= 987 "
Deficit in No. 2 tank	= 9,111 " (3)

(4) The heats of formation of the acid and salts concerned are:

(Ag, N, O ^s , Ag)	= 23,000 cal.	=	213 cal.	per gram Ag.
(Pb, N ^s , O ^s , Ag)	= 98,200 "	=	474 "	" " Pb.
(Cu, N ^s , O ^s , Ag)	= 81,300 "	=	1,278 "	" " Cu.
(Fe, N ^s , O ^s , Ag)	= 43,900 "	=	784 "	" " Fe.
(H, N, O ^s , Ag)	= 48,800 "	=	48,800 "	" " H

The heat balance per 100 grams of anodes No. 1 is:

Solution of Ag, 98.66 ×	213	=	21,015 cal.
" Pb, 1.09 ×	474	=	517 "
" Cu, 0.12 ×	1,278	=	153 "
" Fe, 0.09 ×	784	=	71 "
Heat evolved		=	21,756 cal.
Deposition of Ag, 93.99 ×	213	=	20,020 "
Liberation of H ^s 0.06 ×	48,800	=	2,928 "
Heat absorbed		=	22,948 "
Heat deficit		=	1,192 "

Since this is per 25 ampere-hours [see (2)] and 1 ampere hour at 1 volt = 860 calories, the voltage which this deficit of energy will absorb in the case of anodes No. 1 is:

$$1,192 \div 25 \div 860 = 0.06 \text{ volt.} \quad (4)$$

The similar calculation for anodes No. 2 gives per 100 grams corroded:

Solution of Ag, 77.94 ×	213	=	16,601 cal.
" Pb, 3.70 ×	474	=	1,754 "
" Cu, 20.19 ×	1,278	=	25,803 "
" Fe, 1.00 ×	784	=	784 "
Heat evolved		=	44,942 cal.
Deposition of Ag, 98.11 ×	213	=	20,897 "
Liberation of H ^s 0.064 ×	8,800	=	2,928 "
Heat absorbed		=	23,825 "
Surplus heat		=	21,117 "
Voltage <i>generated</i>		=	0.98 volt.

(4)

(5) Resistance of each element of electrolyte of 1 square cm. area is $20 \times 4 = 80$ ohms. The current passing through this is $220 \div 10,000 = 0.022$ amperes. The drop of voltage, due to the resistance of the electrolyte, is, therefore,

$$0.022 \times 80 = 1.76 \text{ volts.}$$

Adding decomposition voltage we have

In case of No. 1 anodes, $1.76 + 0.06$	= 1.82 volts.	
Add for resistance of contacts	0.18 "	
Working voltage	2.00 "	(5)
In case of No. 2 anodes, $1.76 - 0.98$	= 0.78 "	
Add for resistance of contacts	0.18 "	
Working voltage	0.96 "	(5)

(6) Horsepower required per tank:

$$\text{Anodes No. 1: } \frac{220 \times 2.00}{750} = 0.59 \text{ hp.}$$

$$\text{Anodes No. 2: } \frac{220 \times 0.96}{750} = 0.28 \text{ "}$$

Power per kilogram of silver deposited:

$$\begin{aligned} \text{Anodes No. 1, } 0.59 \div 19.85 &= 0.020 \text{ hp-days} \\ &= 0.48 \text{ hp-hours. (6)} \\ \text{Anodes No. 2, } 0.28 \div 19.85 &= 0.014 \text{ hp-days.} \\ &= 0.34 \text{ hp-hours. (6)} \end{aligned}$$

Problem 128.

The Wohlwill process for refining gold bullion operates with AuCl_3 solution, strongly acid with HCl . Design a plant for refining bullion having the analysis:

Au.....	60.3	Fe.....	2.2
Ag.....	7.0	Ni.....	2.0
Cu.....	6.5	Pb.....	7.0
Zn.....	15.0		

Assume the following data to start with:

Current density, 1,000 amperes per square meter.

Use ten tanks in series.

Tanks available, 500 mm. \times 500 mm. \times 300 mm. deep, inside.

Electrodes about 4 cm. apart.

Starting sheets 1 mm. thick.

Anodes 20 mm. thick.

Specific gravity of anodes 17.5.

Gold present in solution 50 grams per liter.

Specific resistance of electrolyte 5 ohms.

Specific gravity of the electrolyte 1.15.

Loss of electromotive force at contacts one-half the loss due to the resistance of the solution.

Anode products, AuCl_3 , AgCl , CuCl , ZnCl_2 , FeCl_2 , NiCl_2 , PbCl_2 .

Required:

- (1) The size and dimensions of electrodes and number in a tank.
- (2) Current used and total voltage of the system.
- (3) Gold deposited per day.
- (4) Anodes corroded per day, assuming corrosion uniform.
- (5) Deficit of gold in the tanks per day.
- (6) If anodes are left in until 9/10 dissolved, how long will they last?
- (7) If cathodes are removed every 24 hours, what is the average time of treatment?
- (8) At 6 per cent per annum, what is the interest charge per kilogram of gold under treatment in the plant, gold being worth 72.9 cents per gram.

Solution:

(1) Allowing 1 cm. clearance at the sides, the plates must not be over 48 cm. in width across the tank. The electrolyte must not be nearer than 2 cm. to the top of the tank, and the plates ought to be 8 centimeters above the bottom, to allow space for slimes to accumulate. The immersed depth of plates is, therefore, ~~40~~⁴⁶ cm., and the superficial area 960 sq. cm. on a side.

With spaces 4 cm., anodes 2 cm. thick and cathodes 0.1 cm., using one more cathode than anode, we have the spaces equal in number to twice the anodes, and, therefore,

$(2 \times \text{anodes}) + (\text{anodes} + 1) 0.1 + (2 \text{ anodes} + 4) = 50$, whence the number of anodes figure out 4.9. (1)

Choosing the nearest whole number, 5, there will be 6 cathodes, and the working spaces will be 10, and their width

$$\frac{50 - 5(2) - 6(0.1)}{10} = 3.94 \text{ cm.} \quad (1)$$

(2) Ignoring the edges of the plates, the working surface per tank is $960 \times 2 \times 5 = 9,600$ sq. cm., and the current $9,600 \div 10,000 \times 1,000 = 960$ amperes. (2)

The voltage to overcome ohmic resistance is

$$\frac{5 \times 3.94}{10,000} \times \left(\frac{1,000}{10,000} \right) = C = 1.97 \text{ volts.}$$

$$\text{Add 50 per cent loss at contacts} = 0.98 \text{ "}$$

$$\text{Sum} = 2.95 \text{ "}$$

The voltage corresponding to the chemical action occurring can be calculated from the energy of formation of the AuCl^3 decomposed minus the energy of formation of the salts formed. More simply, although not so logically, it may be derived from the voltages of decomposition of these compounds, allowing for the proportions of each formed and decomposed. These are:

$$(\text{Au, Cl}^3) = 27,200 \div 3 \div 23,040 = 0.393 \text{ volt.}$$

$$(\text{Ag, Cl}) = 29,000 \div 1 \div 23,040 = 1.257 \text{ "}$$

$$(\text{Cu, Cl}) = 35,400 \div 1 \div 23,040 = 1.536 \text{ "}$$

$$(\text{Zn, Cl}^2) = 113,000 \div 2 \div 23,040 = 2.448 \text{ "}$$

$$(\text{Fe, Cl}^2) = 100,100 \div 2 \div 23,040 = 2.170 \text{ "}$$

$$(\text{Ni, Cl}^2) = 93,900 \div 2 \div 23,040 = 2.037 \text{ "}$$

$$(\text{Pb, Cl}^2) = 77,900 \div 2 \div 23,040 = 1.690 \text{ "}$$

These are the voltages which would be generated at the anode in case each one of these salts was the only salt being formed. But, since we know the exact composition of our anode dissolved, we can calculate the corresponding voltage generated at the anode:

$$\text{Au, } 0.603 \times 0.393 = 0.237 \text{ volt.}$$

$$\text{Ag, } 0.070 \times 1.257 = 0.088 \text{ "}$$

$$\text{Cu, } 0.065 \times 1.536 = 0.101 \text{ "}$$

$$\text{Zn, } 0.150 \times 2.448 = 0.367 \text{ "}$$

$$\text{Fe, } 0.022 \times 2.170 = 0.048 \text{ "}$$

Ni,	$0.020 \times 2.037 = 0.041$	volt.
Pb,	$0.070 \times 1.690 = 0.118$	"
Sum	1.000	"
Absorbed at the cathode	0.393	"
Total voltage generated	0.607	"
Absorbed in electrolyte and connections	2.95	"
Working voltage per tank	2.34	"
Total for the system	23.4	" (2)

(3) Au deposited by 960 amperes in ten tanks per day:

$$0.00001035 \times \frac{197}{3} \times 60 \times 60 \times 24 \times 960 \times 10 = 563,729 \text{ gr.} \\ = 563.729 \text{ kg.}$$

(4) One gram of anode requires for its corrosion:

Au,	$0.603 \div 197$	$\div 3 \div 0.00001035$
Ag,	$0.603 \div 108$	$\div 0.00001035$
Cu,	$0.065 \div 63.6$	$\div 0.00001035$
Zn,	$0.150 \div 65$	$\div 2 \div 0.00001035$
Fe,	$0.022 \div 56$	$\div 2 \div 0.00001035$
Ni,	$0.020 \div 59$	$\div 2 \div 0.00001035$
Pb,	$0.070 \div 207$	$\div 2 \div 0.00001035$

$$= 0.01703 \div 0.00001035 = 1,645 \text{ amp. seconds.}$$

Current available per day:

$$960 \times 60 \times 60 \times 24 \times 10 = 829,440,000 \text{ amp. seconds.}$$

Anodes corroded per day:

$$829,440,000 \div 1,645 = 504,220 \text{ grams.} \\ = 504.220 \text{ kilograms (4)}$$

$$(5) \text{ Gold deposited} = 563.729 \text{ "}$$

$$\text{Gold dissolved} = 504.220 \times 0.603 = 304.045 \text{ "}$$

$$\text{Deficit of gold in the plant per day} = 259.684 \text{ " (5)}$$

(6) Weight of anodes:

$$960 \times \frac{4}{1} \times 17.5 \times 5 \times 10 = 3,360,000 \text{ grams.} \\ = 3,360 \text{ kilograms.}$$

$$\text{One-tenth scrap} = 336 \text{ "}$$

$$\text{Weight corroded} = 3,024 \text{ "}$$

Days to corrode them:

$$\frac{3,024}{504.22} = 5.93 = \text{practically 6 days.} \quad (6)$$

(7) Average time of treatment, removing one-sixth each day:

$$(1+2+3+4+5+6) \div 6 = 3.5 \text{ days.} \quad (7)$$

(8) Value of gold in plant is, in regular running, value of cathodes for all the time plus value of anodes for $3.5 \div 6 = 58$ per cent of the time.

Value of cathodes:

$$960 \times 0.1 \times 19.2 \text{ (sp. gr. gold)} \times 6 \times 10 \times 0.729 = \$80,578$$

Value of gold in anodes:

$$3,360,000 \times 0.603 \times 0.729 = 1,477,012$$

Average value of anode gold under treatment:

$$1,477,012 \times (3.5 \div 6) = 861,590$$

Sum of cathode gold continually in stock and average value of anode gold under treatment:

$$\$80,578 + \$861,590 = \$942,168$$

$$\text{Interest per annum at 6 per cent} = 56,530$$

$$\text{Interest charge per day} = 155$$

Interest charge per kg. of anode refined:

$$\$155 \div 504.22 = \$0.31 \text{ per kg.}$$

Interest charge per kg. of gold under treatment:

$$\$155 \div 304.045 = \$0.51 \text{ per kg.} \quad (8)$$

THE VOLATILIZATION OF SILVER AND GOLD.

It is known that both of these metals can be vaporized; it can easily be done in the electric arc. If they are placed in a vacuum, in quartz vessels, they show signs of metal vaporizing at 680° and $1,070^\circ$, respectively, although what vapor tension this corresponds to we do not exactly know, but we can surmise it to be a small fraction of a millimeter. If heated still higher in a vacuum, they show the phenomenon of ebullition, or boil, at $1,360^\circ$ and $1,800^\circ$, respectively, although here again we do not know what pressure this corresponds to,

except it is the pressure of the melted metals above the spot where the vapor commences to form beneath the surface, which might be 5 to 10 millimeters of melted metal, say 10 millimeters of mercury, if the bath of metal were shallow.

From these data, obtained by Schuller, Krafft and Bergfeld, it is estimated that the boiling points of the two metals under atmospheric pressure are 2,040° and 2,530°, respectively, on the assumption that the temperature interval between first signs of vaporization in a vacuum and boiling in a vacuum is equal to the interval between the latter temperature and the ordinary boiling point. (This is said to be true of mercury.)

O. P. Watts has estimated the boiling point of silver and gold as 1,850° and 2,800°, respectively, meaning probably at atmospheric pressure; but his estimate is based on such assumptions that they cannot lay claim to as much accuracy as the data and estimates above cited.

If we go back to the very probable rule, that at equal fractions of the normal boiling points, expressed in absolute temperatures, metals have the same vapor tensions, we can compare silver and gold with mercury, whose vapor tension is known through a wide range, and get quite probable values for the vapor tensions of these metals through a large range of temperature. The following table is from nearly zero tension to about the temperature at which ebullition is noticeable in a vacuum:

<i>Tension of Vapor. mm. of Hg.</i>	<i>Mercury. C°</i>	<i>Lead. C°</i>	<i>Silver. C°</i>	<i>Gold. C°</i>
0.0002	0	625	729	942
0.0005	10	658	766	987
0.0013	20	691	802	1,031
0.0029	30	724	839	1,075
0.0063	40	757	876	1,120
0.013	50	790	913	1,165
0.026	60	822	949	1,209
0.050	70	855	986	1,254
0.093	80	888	1,023	1,298
0.165	90	921	1,059	1,343
0.285	100	954	1,096	1,387

<i>Tension of Vapor. mm. of Hg.</i>	<i>Mercury. C°</i>	<i>Lead C°</i>	<i>Silver. C°</i>	<i>Gold. C°</i>
0.478	110	987	1,133	1,432
0.779	120	1,020	1,169	1,476
1.24	130	1,053	1,206	1,520
1.93	140	1,086	1,243	1,565
2.93	150	1,119	1,280	1,611
4.38	160	1,151	1,316	1,654
6.41	170	1,184	1,353	1,699
9.23	180	1,217	1,390	1,743

Inspecting the above table, we see that apparently about 0.0002 mm. of mercury tension is sufficient to make a metal show signs of vaporization. The corresponding temperatures at which silver and gold show 0.0002 mm. tension are, from the above table, 729° and 942°, respectively, whereas it is said to have been observed for these metals at 680° and 1,070°. The divergence is not wide, considering the lack of exact data involved.

Mercury is said to show ebullition in a vacuum at 180°, lead at 1,250°, silver at 1,360° and gold at 1,800°. From the above table we see these metals having the same vapor tension at 180°, 1,217°, 1,390°, and 1,743°, respectively. The agreement is encouraging.

The table in continuation is for temperatures from those causing ebullition in a vacuum to those required to boil the metals at atmospheric pressure:

<i>Tension of Vapor. mm. of Hg.</i>	<i>Mercury. C°</i>	<i>Lead. C°</i>	<i>Silver. C°</i>	<i>Gold. C°</i>
9.23	180	1,217	1,390	1,743
14.84	190	1,250	1,427	1,788
19.90	200	1,283	1,463	1,832
26.35	210	1,316	1,500	1,877
34.70	220	1,349	1,537	1,921
45.35	230	1,382	1,574	1,965
58.82	240	1,415	1,610	2,010
75.75	250	1,448	1,647	2,055
96.73	260	1,480	1,684	2,099

<i>Tension of Vapor. mm. of Hg.</i>	<i>Mercury. C°</i>	<i>Lead. C°</i>	<i>Silver. C°</i>	<i>Gold. C°</i>
123.	270	1,513	1,720	2,144
155.	280	1,546	1,757	2,188
195.	290	1,579	1,794	2,233
242.	300	1,612	1,830	2,277
300.	310	1,645	1,867	2,322
369.	320	1,678	1,904	2,366
451.	330	1,711	1,941	2,410
548.	340	1,744	1,977	2,455
663.	350	1,777	2,014	2,500
760.	357	1,800	2,040	2,530

For tensions of metallic vapors over 1 atmosphere, such as may easily occur in high temperature work, particularly in electric furnaces, the following data may be useful:

<i>Tension of Vapor. Atmospheres.</i>	<i>Mercury. C°</i>	<i>Lead. C°</i>	<i>Silver. C°</i>	<i>Gold. C°</i>
1.0	357	1,800	2,040	2,530
2.1	400	1,951	2,197	2,722
4.25	450	2,116	2,380	2,945
8.	500	2,280	2,564	3,167
13.8	550	2,445	2,747	3,390
22.3	600	2,609	2,931	3,612
34.0	650	2,774	3,114	3,835
50.	700	2,938	3,298	4,057
72.	750	3,103	3,481	4,280
102.	800	3,267	3,665	4,502
137.5	850	3,436	3,848	4,725
162.	880	3,525	3,958	4,858

The last table may not be of much immediate practical value, but it is interesting scientific information. The preceding tables are, however, technically and commercially important. They point particularly to the wastefulness of melting silver or gold in open furnaces where furnace gases pass over the metal. Such gases, at temperatures above 700° for silver and 950° for gold, *i.e.*, even passing over *unmelted* metal, can cause volatilization and loss of weight, because they

evaporate the metal on exactly the same principle that a current of dry air evaporates ice or water. They also explain why silver volatilizes with lead in the cupellation operation. At 1,000° C. lead has a vapor tension of about 0.62 mm. of mercury, and silver about 0.07 mm., and therefore, a considerable loss of silver is sure to occur with the lead vapors passing off. Gold at the same temperature has only 0.0007 mm. tension, and, therefore, proportionately less of it is lost, say only one-fiftieth as much as the silver loss, reckoning from the proportionate tensions and the relative densities of the two vapors.

In calculating such metallic vapor losses it is important to remember that the metals are monatomic when in the state of vapor, and that the molecular weights of their vapors are simply their atomic weights. The hypothetical weight of a cubic meter of such metallic vapor at standard conditions, 0° C. and 760 mm. pressure, is therefore,

$$0.09 \text{ kg.} \times \frac{\text{atomic weight}}{2},$$

and from this theoretical datum the weight of *any* volume at *any* temperature and *any* tension can be calculated.

Illustration: Calculate the weight of silver vapor contained in 1 cubic meter of furnace gases, if saturated with silver vapor and at 1,100° C.

Solution: Since the tension of silver at this temperature is 0.28 mm., the question resolves itself into this: What is the weight of 1 cubic meter of silver vapor at 1,100° and 0.28 mm. pressure. One cubic meter at standard conditions would be $0.09 \times (108 \div 2) = 4.86$ kilograms; therefore, at these given conditions, it contains:

$$4.86 \times \frac{273}{1,100 + 273} \times \frac{0.28}{760} = 0.0035 \text{ kg.}$$

$$= 3.5 \text{ grams.}$$

It is true that the silver vapor, being heavy, mixes slowly with the furnace gases, but, nevertheless, the gases rushing over and coming in contact with the silver may become nearly saturated with this vapor, and carry considerable away. In

the Bessemerizing of copper matte to blister copper, by blowing air directly through it, as much as 30 per cent of all the silver present may be thus vaporized from the bath as soon as the silver has taken the metallic form.

Every smelter and refiner of the precious metals should be familiar with these facts, and draw conclusions from them useful to the conduct of his business.

The specific heat of these metallic vapors is 0.225 per cubic meter (calculated to standard conditions), and the latent heat of vaporization is approximately twenty-three times the normal boiling point expressed in absolute temperature for one atomic weight of the metal—as explained in Part I of these calculations.

For silver and gold we would have the latent heats:

$$\begin{array}{rcll} \text{Ag, 23 (2,040 + 273)} & = & 53,200 \text{ Cal. per 108 kg.} \\ & = & \mathbf{493} & \text{" 1 kg.} \\ \text{Au, 23 (2,530 + 273)} & = & 64,470 & \text{" 197 kg.} \\ & = & \mathbf{327} & \text{" 1 kg.} \end{array}$$

The above latent heats of vaporization are for boiling at normal atmospheric pressure; for vaporization at other pressures and corresponding temperatures, correction must be made for the difference in specific heats of the metallic vapor and liquid metal.

CHAPTER IV.

THE METALLURGY OF ZINC. (INCLUDING CADMIUM AND MERCURY.)

At the present time, the metallurgy of zinc is briefly comprehended in the following statements: The chief ore is zinc sulphide, ZnS , infusible at ordinary furnace heats, non-volatile, easily roasted to ZnO ; the roasting is done principally in mechanically stirred furnaces, the ore being in small pieces, because it is non-porous, compact, and roasts slowly; the roasted ore, principally ZnO , is mixed with an excess of carbon as a reducing agent, and heated in closed fire-clay retorts having condensers attached; zinc vapors begin to come off at 1033°C. , and come off rapidly at the working temperature of the charge, say 1200° to 1300° ; the zinc vapor and carbon monoxide pass into the condensers, and as they cool deposit the zinc, some in the form of fine dust (like hoar frost), most of it as liquid drops; the cadmium in the ore and some lead, if present, distil over with the zinc, constituting its chief impurities. Arsenic is sometimes present in the condensed product. Iron does not distil over, but some is absorbed from ladles and moulds in which the liquid zinc may be handled and cast.

The chief operations with which calculations may be concerned are the roasting, reduction by carbon, condensation of the vapors, possibility of blast-furnace extraction, of electric furnace reduction, electrolytic extraction, electrolytic refining.

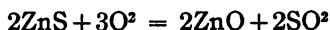
Roasting of Sphalerite.

Before roasting, the crude ore is crushed and concentrated. Pure ZnS contains 67 per cent zinc and 33 per cent sulphur; its specific gravity is 3.9 and it has fine cleavage, so that it crushes easily, producing much fines or slimes. In the Joplin district, in Missouri, the largest zinc field in America, the ore as mined averages some 4.3 per cent of zinc, equal to 6.4 per cent of pure blende, ZnS , and is concentrated by jigging to

heads carrying about 60 per cent of zinc (90 per cent of ZnS), containing some 70 per cent of the zinc in the ore, and tails carrying about 1.35 per cent of zinc (2 per cent of ZnS), representing 30 per cent of the zinc in the ore. The concentrates average 5 per cent of the weight of the ore; concentration ratio 20 to 1. Cost of such crushing and concentration 20 to 40 cents per ton of ore milled. (Ingalls.) The average composition of these concentrates is:

Zinc.....	60 per cent	= 90 per cent ZnS.
Iron.....	2 "	= 3 per cent FeS.
Silica.....	7 "	
Sulphur.....	31 "	
	<hr/>	
	100	

Zinc sulphide begins to be oxidized by air at a dull red heat, say, 600° C., and if the supply of air is kept up the oxidation is rapid, generating a large amount of heat and consequent high temperature.



The question as to how high a temperature would theoretically result if sphalerite were thus burned is an interesting one. Ingalls quotes Hollaway as giving 1992° C. We will investigate this point as being of interest and value in connection with practical roasting.

Problem 129.

Pure ZnS is oxidized by air. The heats of formation concerned are:

$$(\text{Zn}, \text{S}) = 43,000$$

$$(\text{Zn}, \text{O}) = 84,000$$

$$(\text{S}, \text{O}^2) = 69,260$$

The specific heats of the materials concerned are:

Sm to O°

$$\text{Zn S} = 0.120 + 0.00003t$$

$$\text{Zn O} = 0.1212 + 0.0000315t$$

$$\text{S O}^2 (1 \text{ m}^3) = 0.36 + 0.0003t$$

$$\text{O}^2 \text{ or N}^2 (\text{ " }) = 0.303 + 0.000027t$$

Assuming that the blende is first heated to 600°, to start the roasting, and then the air supply put on, the exposed roasting

surface being sufficient for rapid oxidation, and the temperature too high to form SO^3 :

Required:

(1) The theoretical temperature at the roasting surface at starting, if all the oxygen passing is utilized.

(2) The same, when the operation has continued to its maximum temperature.

(3) The same, if three-fourths the oxygen passing is utilized.

(4) The same, if half the oxygen passing is utilized.

(5) The same, if the resulting gases contain only 5 per cent of SO^2 gas.

Solution:

(1) The reaction gives, thermally:

Decomposition of ZnS	—43,000 Cal.
Formation of ZnO	+ 84,800 "
" " SO^2	+ 69,260 "
<hr/>	
Net heat evolution	111,060 Cal.

This would be concerned in the oxidation of 97 kg. of ZnS to 81 kg. of ZnO and 64 kg. of SO^2 ($= 22.22 \text{ m}^3$), and requiring $3 \times 16 = 48$ kg. of $\text{O}^2 = 208$ kg. of air (containing 160 kg. = 127 cubic meters of N^2).

Heat in 97 kg. of ZnS at $600^\circ = 8,032$ Cal.

Total heat in the products = 119,092 "

Mean heat capacity of the products per 1° , from 0° to t° :

81 kg. ZnO	=	$9.8172 + 0.002552t$
$22.22 \text{ m}^3 \text{ SO}^2$	=	$8.0000 + 0.006667t$
$127 \text{ m}^3 \text{ N}^2$	=	$38.4810 + 0.003429t$
<hr/>		
Sum	=	$56.2982 + 0.012648t$

Therefore, theoretical surface temperature, at starting,

$$t = \frac{119,092}{56.2982 + 0.012648t} = 1565^\circ \text{ C.} \quad (1)$$

(2) When the surface of the oxidizing material has attained its maximum temperature, it is practically at t° , and the products of combustion will contain 111,060 Calories plus the heat in 97 kg. of ZnS at t° . We then have

$$t = \frac{111,060 + 11.24t + 0.00291t^2}{56.2982 + 0.012648t} = 1780^\circ. \quad (2)$$

It must be emphasized that this is the theoretical maximum under the most favorable conditions as to oxidation and exact air supply, conditions never realized in practice.

(3) The excess of oxygen would be $48 \times \frac{1}{3} = 16 \text{ kg.} = 11.11 \text{ m}^3$. This would be the most favorable possible proportion for making sulphuric acid from the gases, since it would just serve to oxidize the SO^2 to SO^3 in the acid chambers, the complete reactions being:



The 11.11 m^3 of oxygen corresponds to 53.4 m^3 of excess air, whose mean heat capacity is $16.1903 + 0.001443t$. Adding this to the mean heat capacity of the products we have:

$$t = \frac{111,060 + 11.24t + 0.00291t^2}{72.4885 + 0.014091t} = 1437^\circ \quad (3)$$

(4) This is more nearly the practical conditions, and applying the principles above explained, we have:

$$t = \frac{111,060 + 11.24t + 0.00291t^2}{104.8691 + 0.016977t} = 1027^\circ \quad (4)$$

(5) If the gases contain 5 per cent of SO^2 gas, their total volume per formula weight of SO^2 produced, in kilograms, is:

$$22.22 \div 0.05 = 444.4 \text{ m}^3$$

and the volume of excess air they contain is:

$$444.4 - 22.2 - 127 = 295.2 \text{ m}^3$$

the heat capacity of this excess air, per average 1° is:

$$89.4456 + 0.007970t$$

and

$$t = \frac{111,060 + 11.24t + 0.00291t^2}{145.7438 + 0.024947t} = 731^\circ \quad (5)$$

It follows from this analysis and these results, that effective auto-roasting of zinc sulphide is practicable provided that the ore is finely divided, so as to expose large surface, oxidize quickly, and utilize the oxygen of the air efficiently. Without these conditions, auto-roasting is impracticable.

It ought to roast satisfactorily by pot roasting, if the proper conditions as to size of ore, speed of blast, thickness of pot walls, etc., can be found.

Problem 130.

Average blende concentrates, containing 90 per cent ZnS, 3 per cent FeS, 7 per cent SiO_2 , are roasted by the use of 30 per cent of coal, in a furnace with a hearth 135 feet effective length, the unroasted sphalerite remaining being 2.6 per cent of the roasted material. The iron is roasted to Fe_2O_3 . The coal carries 75 per cent of carbon, 5 per cent of hydrogen, 8 per cent of oxygen, 1 per cent of sulphur and 11 per cent of ash. The chimney gases average 2 per cent of SO_2 and escape from the furnace at 300°C . Charge is drawn from the furnace at 1000°C . Furnace roasts 40,000 pounds per day. Width of furnace, 12 feet; height, 8 feet.

Required:

- (1) The composition of the roasted ore.
- (2) The heat generated by the roasting of 2,000 pounds of the ore.
- (3) The heat generated by the combustion of the fuel.
- (4) The heat in the hot charge as drawn.
- (5) The heat in the chimney gases.
- (6) The heat lost by radiation and conduction.
- (7) The heat loss calculated to pound-calories per square foot of outer surface per minute.

Solution:

(1) The 2.6 per cent of ZnS in the roasted ore is per cent of it, and not of the raw ore. The simplest method of getting the composition of the roasted ore is to represent by x the quantity of ZnS remain unoxidized per 100 of raw ore. We then have:

Weight of ZnS oxidized, per 100 raw ore $= 90 - x$

$$\text{“ “ ZnO formed} = (90 - x) \times \frac{81}{97} = 75.2 - 0.835 x$$

$$\text{“ “ Fe}_2\text{O}_3 \text{ “} = 3 \times \frac{160}{176} = 2.7$$

Weight of SiO_2 remaining	= 7.0
" " roasted ore	= $84.9 - 0.835 x$
" " " " also	= $x \div 0.026$

Therefore

$$84.9 - 0.835 x = x \div 0.026$$

Whence

$$x = 2.2$$

Percentage of the ZnS oxidized

$$\frac{90 - 2.2}{90} = 0.976 = 97.6 \text{ per cent.}$$

Composition and weight of the roasted ore:

ZnS	= 2.2 = 2.6 per cent.
ZnO	= 73.4 = 86.1 "
Fe_2O_3	= 2.7 = 3.1 "
SiO_2	= 7.0 = 8.2 "

Weight	<u>85.3</u>
--------	-------------

Zinc contents = 60.0 = **70.3** per cent. (1)

(2) Zinc sulphide oxidized to ZnO

$$2000 \times (0.90 - 0.022) = 1,756 \text{ lbs.}$$

Heat of oxidation of 97 lbs. of ZnS to

ZnO and SO_2 (from Prob. 129) = 111,060 lb.-Cal.

Heat of oxidation of 1 lb. = 1,145 " "

" " " " 1,756 lbs. = 2,010,620 " " (2)

(3) Heat of combustion of 1 lb. of fuel to CO_2 and H_2O vapor:

C to CO_2 0.75×8100 = 6075 lb.-Cal.

Available Hydrogen

$$0.05 - 0.01 = 0.04$$

H to H_2O condensed

$$0.04 \times 34,500 = 1380 \text{ " "}$$

Calorific power to H_2O condensed = 7455 " "

Water formed

$$0.05 \times 9 = 0.45$$

Latent heat of condensation

$$0.45 \times 606.5 = 273 \text{ " "}$$

Calorific power to H_2O vapor

$$= \underline{7182} \text{ " "}$$

$$\begin{array}{rcl}
 \text{Coal used per 2000 lbs. of ore} & = & 600 \text{ lbs.} \\
 \text{Calorific power} = 600 \times 7182 & = & 4,309,200 \text{ lb.-cal.}
 \end{array}
 \quad (3)$$

$$\begin{array}{rcl}
 \text{Total heat generated in the furnace} & & \\
 2,010,620 + 4,309,200 & = & 6,319,820 \text{ " "}
 \end{array}$$

$$\begin{array}{rcl}
 \text{Proportion of total generated by the roasting} & & \\
 2,010,620 \div 6,319,820 & = & 0.325 = 32.5 \text{ per cent.}
 \end{array}$$

(4) Charge, as drawn, per 2000 lbs. of raw ore:

$$\begin{array}{rcl}
 \text{ZnS} & 44 \text{ lb.} & \\
 \text{ZnO} & 1468 \text{ "} & \\
 \text{Fe}^2\text{O}^3 & 54 \text{ "} & \\
 \text{SiO}^2 & 140 \text{ "} & \\
 \hline
 & 1706 \text{ "} &
 \end{array}$$

Heat in this, at 1,000° C.

$$\begin{array}{rcl}
 \text{ZnS} & 44 \times 0.150 & = 6.6 \\
 \text{ZnO} & 1468 \times 0.153 & = 224.6 \\
 \text{Fe}^2\text{O}^3 & 54 \times 0.344 & = 18.0 \\
 \text{SiO}^2 & 140 \times 0.260 & = 36.4
 \end{array}$$

$$285.6 \times 1000 = 285,600 \text{ lb.-Cal.} \quad (4)$$

(5) Sulphur going into the gases:

$$\begin{array}{rcl}
 \text{S from ZnS} & = 1756 \times 32/97 & = 579.4 \text{ lb.} \\
 \text{S " FeS} & = 60 \times 32/88 & = 21.8 \text{ "} \\
 \text{S " coal} & = 600 \times 0.01 & = 6.0 \text{ "}
 \end{array}$$

$$\begin{array}{rcl}
 \text{Weight of S} & = & 607.2 \text{ "} \\
 \text{" " O for SO}^2 & = & 607.2 \text{ "} \\
 \hline
 \text{" " SO}^2 & & 1214.4 \text{ "}
 \end{array}$$

$$\begin{array}{rcl}
 \text{Volume of SO}^2\text{—} & & \\
 (1214.4 \times 16) \div 2.88 & = & 6,747 \text{ cubic feet.}
 \end{array}$$

$$\begin{array}{rcl}
 \text{Volume of chimney gas—} & & \\
 6,747 \div 0.02 & = & 337,350 \text{ " "}
 \end{array}$$

$$\begin{array}{rcl}
 \text{Volume of CO}^2 \text{ in it—} & & \\
 (600 \times 0.75 \times 16) \div 1.98 & = & 3,636 \text{ " "}
 \end{array}$$

$$\begin{array}{rcl}
 \text{Volume of H}^2\text{O in it—} & & \\
 (600 \times 0.45 \times 16) \div 0.81 & = & 5,333 \text{ " "}
 \end{array}$$

$$\begin{array}{rcl}
 \text{Volume of N}^2 \text{ and excess air} & = & 321,634 \text{ " "}
 \end{array}$$

Heat in these gases at 300° C.

CO ²	$3,636 \times 0.436 =$	1,585	oz.-cal. per 1°	
H ² O	$5,333 \times 0.385 =$	2,057	" " "	
SO ²	$6,747 \times 0.450 =$	3,036	" " "	
N ² and O ²	$321,634 \times 0.311 =$	100,028	" " "	
		106,706	" " "	
		= 6,669 lb.-Cal.	"	
		= 2,000,700	" " 300°	(5)

(6) Summary of heat distribution:

Heat available, per 2,000 lb. ore = 6,319,820 lb.-Cal.

Heat in hot ore drawn,	235,600	" "	
" " chimney gases,	2,000,700	" "	
Loss by radiation and conduction,	4,083,620	" "	
	6,319,820	" "	(6)

(7) Approximate periphery of furnace:

$$12 + 12 + 8 + 8 = 40 \text{ feet.}$$

Approximate outer surface, including base:

$$40 \times 135 = 5,400 \text{ sq. feet.}$$

Ore roasted per hour:

$$40,000 \div 24 = 1,667 \text{ lb.}$$

Heat radiated and conducted away per hour:

$$\frac{4,083,520}{2,000} \times 1,667 = 3,360,000 \text{ lb.-Cal.}$$

Per square foot outside area, per hour:

$$3,360,000 \div 5,400 = 622 \text{ lb.-Cal.}$$

$$\text{per minute} = 10.5 \text{ " " (7)}$$

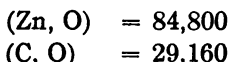
Reduction of Zinc Oxide.

Since metallic zinc boils under atmospheric pressure at 930° C., and carbon does not begin to reduce zinc oxide until 1033° is reached, the zinc reduced is necessarily obtained in the state of vapor. To make the reaction proceed fast, a temperature of the charge inside the retorts of 1100° to 1300° C. at the end

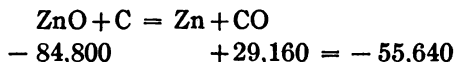
is necessary. A large amount of heat is absorbed in the reaction, which must be supplied as a current or flow of heat through the walls of the retort in order to keep the reaction and reduction going. Since the walls of the retort are fire-clay, averaging 4 centimeters (1.6 inch) thick, there must be a considerable difference of temperature (temperature head) between the inside and outside of the retort in order to keep up the flow of heat inward.

THERMOCHEMICAL CONSIDERATIONS.

The heat of formation of zinc oxide, at ordinary temperatures, is 84,800 Calories for a molecular weight, 81 kilos, of oxide, as determined by thermochemical experiment. This means that cold zinc uniting with cold oxygen, and the hot product cooled down to the same starting temperature, results in the evolution of heat stated. Cold carbon uniting with cold oxygen to cold carbonous oxide, CO, gives similarly 29,160 Calories per molecular weight, 28 kilograms, of gas formed. These facts are expressed thermochemically as



The equation of reduction becomes



This means that if we start with cold zinc oxide and cold carbon, the heat absorbed is 55,640 Calories ending up with cold products, zinc and CO at ordinary temperatures.

What is actually done in practice, however, is to first heat the ZnO and C to a high temperature, at least to 1033°, and then to supply the heat of the reaction at that temperature, producing zinc vapor and CO gas, both at 1033°. The process of reduction, therefore, resolves itself plainly into two steps: (1) heating the charge up to the reacting temperature, (2) supplying the latent heat of the chemical change at that temperature.

Heating up the Charge.

The charge usually contains more carbon than is theoretically necessary for reduction of the zinc oxide, because some is consumed by air in the retort, some in reducing iron oxides and

some is left behind unused; it is cheaper to lose carbon than unreduced zinc oxide. However, making the calculation on the theoretical amount of carbon only (anyone can modify it for any excess of carbon used in any specific case) we need to know the heat necessary to raise these reacting substances to the temperature of reaction.

The heat in 1 kilogram of zinc oxide at various temperatures was determined in the writer's laboratory as $0.1212t + 0.0000315t^2$. The heat in 1 kilogram of carbon at temperatures above 1000° is represented by $0.5t - 120$. We have the heat necessary to raise our 81 kilograms of ZnO and 12 kilograms of carbon to 1033° as

$$\begin{aligned} \text{ZnO} : 0.1212 (1033) + 0.0000315 (1033)^2 \times 81 \\ = 159 \times 81 = 12,879 \text{ Cal.} \\ \text{C} : [0.5 (1033) - 120] \times 12 = 396 \times 12 = 4,752 \text{ "} \\ \hline \text{Sum} = 17,631 \text{ "} \end{aligned}$$

This quantity represents the heat per 81 of oxide and 12 of carbon, or 93 of charge containing 65 of zinc. Per 1000 kilograms of oxide, containing 800 kilos of zinc, it would be

$$17,631 \times \frac{1000}{81} = 217,670 \text{ Calories.}$$

It should be noted that this quantity is actually proportional to the weight of the charge, ore plus reducing agent, and independent of the amount of zinc in it. A ton of poor ore will practically require as much heat to bring it up to the reaction temperature as a ton of rich ore, so that these costs are proportional to the weight of charge treated and not to the weight of zinc it contains.

If the charge is heated electrically, the amount of electric power needed for heating up can be calculated, assuming an average loss of 10 to 30 per cent of the total heat by radiation and conduction from the furnace.

Illustration:

A retort contains 300 kilograms of charge mixture and is heated electrically to 1033° , the reaction temperature at an efficiency of 75 per cent, by an electric current of 250 horse-power. How long will the heating-up period last.

Solution:

Heat needed in the charge, $217,670 \times 0.3 = 65,300$ Calories.
 Heat to be supplied $= 65,300 \div 0.75 = 87,070$ Calories. Power applied supplies $635 \times 250 = 158,750$ Calories per hour. Time required $87,070 \div 158,750 = 0.55$ hour $= 33$ minutes.

If the charge is heated by furnace gases outside the retort we must take into consideration that the fire-clay is a poor conductor, that the rate of transmission of heat through the walls falls off as the charge becomes hot, and that the outside surface of the retort must be kept well above 1033° in order to get the charge to that temperature in a reasonable time. The conductance of fire-clay for high temperature is 0.0031; that is, 0.0031 gram-calories pass through each square centimeter per second, if one centimeter thick, per 1° C. difference of temperature. When the charge is cold, the inner surface of the retort may be reduced in temperature to a low red heat, say, 500° , and towards the end of the heating-up period its temperature becomes at least 1033° , while the outer surface is kept continually at 1200° , let us say, by the furnace gases. During the heating-up period there is a difference of temperature producing heat flow of 700° , for a short time, down to, say, 200° , which we may average up as 300° heat difference. The heat conductivity of the material of the retort and the thickness of its walls have everything to do with the rate at which the heat can get through and the charge be heated up to the reaction temperature.

Problem 131.

An oval zinc retort is 130 centimeters long, 30 centimeters diameter outside, one way, and 15 centimeters the other, and its walls are 3 centimeters thick. It is charged with 30 kilograms of ore and 12 kilograms of reduction material. The temperatures of the charge in the retort and of the gases outside the retort were as follows:

	In Retort	Outside	Difference
At starting.	0°C.	1067°C.	1067°C.
In 0.5 hour	350	1067	717
" 1.0 "	600	1067	467
" 1.5 hours	781	1067	286
" 2.0 "	814	1100	286

	In Retort	Outside	Difference
" 2.5 "	869	1100	231
" 3.0 "	924	1110	187
" 3.5 "	957	1155	198
" 4.0 "	935	1166	231
" 4.5 "	935	1138	203
" 5.0 "	946	1144	198
" 5.5 "	946	1155	209
" 6.0 "	979	1166	187
" 6.5 "	1001	1177	176
" 7.0 "	1034	1177	143

Average, 319

Take 159 Calories per kg. as the heat required to bring the ore to 1034° and 396 for the reduction material.

Required:

The average heat conductivity in C. G. S. units of the material of the retorts, in the range given, assuming the inner surface of the retort to be at the same temperature as the charge.

Solution:

Heat passing through the retort walls in 7 hours:

$$159 \times 30 = 4770 \text{ Calories}$$

$$396 \times 12 = 4752 \quad "$$

$$\hline 9522 \quad "$$

$$\text{Per second} = 0.378 \quad "$$

$$= 378 \text{ gram-cal.}$$

Surface of retort:

$$\text{Periphery} \quad \sqrt{30 \times 15} \times 3.14 = 66 \text{ cm.}$$

$$\text{Area of sides,} \quad 66 \times 130 = 8580 \text{ sq. cm.}$$

Heat passing through each square cm. per second

$$378 \div 8580 = 0.044 \text{ cal.}$$

Heat passing per 1° difference

$$0.044 \div 319 = 0.00014 \text{ cal.}$$

Since thickness is actually 3 centimeters, conductance in C. G. S. units is:

$$0.00014 \times 3 = 0.00042.$$

Correction:

This coefficient of conductance is far too low. The reason is that the inner temperature, the temperature of the charge, is always lower than the temperature of the inside surface of the retort, and the difference of temperature between the outer and inner walls of the retort must have been far less than the average, 319°. If we take the coefficient of conductance as determined by experiment for firebrick, viz., 0.0031, then the average difference of temperature between the inner and the outer walls of the retort would be:

$$319 \times \frac{0.00042}{0.0030} = 45^\circ \text{C.}$$

This is more likely, than that the conductance of the retort material should be so extraordinarily low. In fact, we are led to the conclusion that the poor heat conductivity of the charge itself is the chief obstacle to its rapid heating, and that pre-heating of the charge would be very advisable if it could be done by some of the waste heat of the gases leaving the furnace.

Distillation of the Charge.

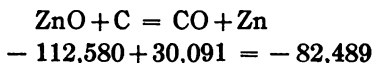
The driving off of the zinc is altogether a different operation from the heating up of the charge to the stated reduction temperature. It is an endothermic chemical operation, comparable to the boiling of water at a constant temperature, the latent heat of the chemical reaction is exactly comparable to the latent heat of vaporization. The temperature must be kept up to the temperature of reduction in order for the reaction to take place at all, and then heat-calories must be supplied at that temperature to keep the reaction going, and the reduction proceeds *pari passu* with the *quantity* of heat supplied at that constant temperature. The question now is: what is the latent heat of this reaction at the reaction temperature.

We must for this purpose know the heat of formation of the substances involved, ZnO and CO, at 1033°. The method of calculating these is too long to insert here, but may be learned from the writer's book on Metallurgical Calculations, Part I, p. 51. We have the heats of formation from the elements as they exist at 1033°:

$$(\text{Zn, O})^{1033} = 112,580$$

$$(\text{C, O})^{1033} = 30,091$$

and the reaction at 1033°



This is seen to be nearly 50 per cent greater than the heat of the reaction calculated to ordinary temperatures, from the ordinary heats of formation as taken from thermochemical tables. The metallurgist should understand this difference, for it is one of the utmost importance in thermochemical calculations, if we want our calculations to represent actual conditions and to check up with practice.

This amount of heat is proportional to the zinc oxide reduced or to the zinc distilled from the charge, but not to the weight of ore charge itself. This requirement will, therefore, be greater, per retort full of material, the richer the charge is in zinc. It is a constant requirement for a given output of zinc, and not per given weight of ore treated.

The heat required for the reduction, therefore, as distinguished from the heating-up period, is

$$\frac{82,489}{81} = 1,018 \text{ Calories per kg. of ZnO reduced}$$

$$\frac{82,489}{65} = 1,269 \quad \text{“} \quad \text{“} \quad \text{“} \quad \text{“} \quad \text{Zn distilled off}$$

$$= 1,269,000 \quad \text{“} \quad \text{“} \quad \text{ton “ “ “ “}$$

Furnishing this reduction heat, at the high temperature required, is the larger part of the heat needed in the whole process. We see that it is some 4.7 times the amount of heat needed to raise the materials to the reduction temperature.

Problem 132.

The retort charge of Problem 131 was kept at the reduction temperature for 14 hours, the temperature outside the retort being gradually raised to 1300° and the average difference in temperature between the gases and the charge being 147°, and there being distilled from the charge in that time 18 kilograms of zinc.

Required:

The average heat conductance in C. G. S. units of the material of the retort from the above data and assumptions.

Solution:

The heat furnished in the 14 hours was as follows:

$$1,269 \times 18 = 22,842 \text{ Calories.}$$

Heat furnished per hour:

$$22,842 \div 14 = 1,632 \quad "$$

Heat furnished per second:

$$\begin{aligned} &= 0.453 \quad " \\ &= 453 \text{ calories} \end{aligned}$$

Heat passing each sq. cm. of retort surface per second:

$$453 \div 8,580 = 0.053 \text{ calories.}$$

Per 1° difference:

$$0.053 \div 147 = 0.00036 \quad "$$

Conductance, in C. G. S. units:

$$0.00036 \times 3 = 0.00108$$

Remarks: This conductance calculates out 2.5 times as great as from the data on the heating-up period, the reason of the higher value being that the charge is at nearly uniform temperature during this reduction period, and therefore the difference between the temperature taken in the middle of the charge and the true temperature of the inner walls of the retort is less than before, and the error from this source less. If we make the same assumption as in the correction to the previous problem, *i.e.*, take the conductance of the retort material as 0.0030, the difference in temperature of the outer and inner walls of the retort during this period would calculate out

$$\frac{147 \times 0.00108}{0.0030} = 53^{\circ}$$

while the center of the charge was then $147 - 53 = 94^{\circ}$ cooler, on an average, than the inner wall of the retort from which it was deriving its heat.

These figures appear reasonable, and the writer would con-

clude, from the data so far available, that the conductance 0.003 probably represents a good approximation to the correct value for zinc retort material, but that, in order to use it, we should have more experimental data as to the average difference between the temperature of the inner walls of the retort and the temperature of the charge at various points in the retort.

Problem 133.

A zinc ore containing 50 per cent of zinc is mixed with 40 per cent of its weight of small anthracite coal, and retorted in a Belgian furnace. The recovery of zinc was 82 per cent of the zinc content of the ore. The consumption of anthracite to heat the furnace was 2.25 tons per 10 of ore. The anthracite contained 90 per cent of carbon and 10 per cent of ash, and had a calorific power of 7500.

Required:

- (1) The total consumption of fuel per 1000 of zinc obtained.
- (2) The efficiency of transfer of heat from the furnace gases to the charge.

Solution:

- (1) Zinc charged, per 1000 of zinc obtained

$$1000 \div 0.82 = 1220$$

Ore charged, per 1000 of zinc obtained

$$1220 \div 0.50 = 2440$$

Coal charged with ore

$$2440 \times 0.40 = 976$$

Coal burned on grate

$$2440 \times 2.25 = 5490$$

Total coal used, per 1000 of zinc obtained

$$976 + 5490 = 6466 \quad (1)$$

- (2) Calorific power of coal burned

$$5490 \times 7500 = 41,170,000$$

Heat required to raise ore to reduction point

$$2440 \times 159 = 387,960$$

Heat required to raise fuel to reduction point

$$\text{Ash } 98 \times 159 = 15,580$$

$$\text{Carbon } 878 \times 396 = 347,690$$

Total to raise charge to reduction point

$$= 751,230$$

Heat absorbed in distilling away 1000 of zinc

$$= 1,269,000$$

Total heat utilized

$$= 2,020,230$$

Thermal efficiency of utilization of the fuel

$$\frac{2,020,230}{41,170,000} = 0.049 = 4.9 \text{ per cent.} \quad (2)$$

Problem 134.

Natural gas from Iola, Kan., has the following composition:

CH ⁴	93	per cent.
H ²	2	"
CO	1	"
C ² H ⁴	1	"
N ²	3	"

It is used in a zinc retort furnace, at an efficiency of transfer of heat to the charge of 4.9 per cent, as calculated in Prob. 133, working a charge which absorbed 2,000,000 Calories per 1000 kilograms of zinc distilled off.

Required: The volume of natural gas required to be used to displace the anthracite fuel used per 1000 kilograms of zinc produced. The cubic feet of gas per 1000 lbs. of zinc produced.

Solution:

Calorific power of the gas

CH ⁴	0.93	× 8623	= 8009
H ²	0.02	× 29030	= 581
C ² H ⁴	0.01	× 14365	= 144
CO	0.01	× 3062	= 31
			<hr/> 8765

This result may be called Calories per cubic meter of gas, or ounce-calories (1° C.) per cubic foot according to whether it is desired to work in metric units or the English system.

Cubic meters of gas required, per 1000 kilograms of zinc produced:

$$\frac{2,000,000}{0.049} + 8765 = 4,700 \text{ cubic meters.}$$

Per 1000 lbs. of zinc produced:

$$\frac{2,000,000}{0.049} \times 16 \div 8765 = 75,200 \text{ cubic feet.}$$

Electric Smelting of Zinc Ores.

In an interesting communication to the *American Electrochemical Society* (Vol. XII, p. 117), Gustave Gin calculates the electric power necessary for the smelting of several varieties of zinc ore, assuming that the zinc vapor and other gases pass out of the furnace at the usual high temperature— 1200° C.

Mr. Gin makes his calculations of heat required on the basis of molecular weight of zinc compound reduced; that is, for 81 parts of ZnO and 65 parts of Zn. Calculating to 1200° , he finds the heat in the products Zn and CO to be

In 65 parts Zn.....	26,720 Cal.
“ 28 “ CO.....	8,280 “
Sum.....	35,000 Cal.

whereas we calculate for the same quantities

In 65 parts Zn.....	37,695 Cal.
“ 28 “ CO.....	8,945 “
	46,640 Cal.

The difference between these numbers is principally in the latent heat of vaporization of zinc, which Gin assumes as 15,370 Calories, but which by a method of evaluation used by the writer figures out 27,670 Calories, and almost exactly the same value has been obtained by a different method by W. McA. Johnson.

Assume then, that we start with cold materials and end with

the products of the reaction leaving the retort at 1200°, the sum total of usefully applied heat is the heat of the reaction calculated at ordinary temperature plus the sensible heat of the products at 1200°, or

Heat absorbed by reaction, ordinary temperature....	84,800 Cal.
Heat in necessary products, at 1200°.....	46,640
Total.....	131,440 "

To this must be added the sensible heat in the residue left in the retort, to get the total heat which has been applied to the charge. If the charge were pure ZnO, with the theoretical amount of carbon, the residue would be *nil*, but in practice there is always a residue of gangue with unused carbon.

Mr. Gin, having calculated the heat requirement on the above basis, then makes his calculations of power required per ton of ore smelted in the following ingenious way: The weight of each component of 1000 kg. of ore is divided by its molecular weight, and thus the number of molecular weights of material in one ton of ore determined, which, so to speak, gives a kind of chemical formula for the ore. An example will make this clear.

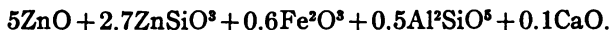
Composition of a calcined calamine zinc ore:

ZnO	40.50 per cent.
ZnSiO ³	38.07 "
Fe ² O ³	9.60 "
Al ² SiO ⁵	8.10 "
CaO	2.80 "

If we divide the weight of each compound present by its molecular weight we get the relative number of molecules present in the ore, and the formula for the ore:

KG. IN 1000 KG.				
ZnO	405	÷ 81	= 5.0	molecular weights.
ZnSiO ³	380.7	÷ 141	= 2.7	"
Fe ² O ³	96.	÷ 140	= 0.6	"
Al ² SiO ⁵	81	÷ 162	= 0.5	"
CaO	28	÷ 56	= 0.1	"

The ore may therefore be represented by the formula



Assuming that the Fe_2O_3 becomes FeSiO_3 , and that there is to be added enough CaO to form CaSiO_3 with the rest of the SiO_2 of the zinc silicate, we will need 1.5 CaO to do it, and since there is 0.1 CaO present, 1.4 CaO must be added, which represents $1.4 \times 56 = 79$ kg. of CaO . To form CO with the oxygen combined with the zinc and iron, reducing the latter to FeO , will require:

for 5	ZnO	5.0 C.
"	2.7 ZnSiO ₃	2.7 "
"	0.6 Fe ₂ O ₃	0.6 "

Sum 8.3 C. = 100 kg.

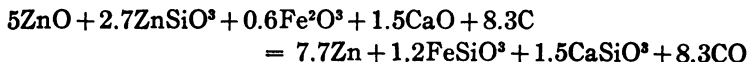
If we use twice the theoretical amount of carbon needed for reduction we have the following balance sheets; weight in kilograms being enclosed:

ORE		ADDED		CHARGE	
5 ZnO	(405)		5 ZnO	(405)
2.7 ZnSiO ₃	(381)		2.7 ZnSiO ₃	(381)
0.6 Fe ₂ O ₃	(96)		0.6 Fe ₂ O ₃	(96)
0.5 Al ₂ SiO ₅	(81)		0.5 Al ₂ SiO ₅	(81)
0.1 CaO	(28)	1.4 CaO	(79)	1.5 CaO	(79)
		16.6 C	(200)	16.6 C	(200)

The distribution of this charge will be as follows:

CHARGE.		GASES.		RESIDUE.	
5 ZnO	(405)	5 Zn	(325)	
2.7 ZnSiO ₃	(381)	2.7 Zn	(175)	
0.6 Fe ₂ O ₃	(96)			1.2 FeSiO ₃	(158)
0.5 Al ₂ SiO ₅	(81)			0.5 Al ₂ SiO ₅	(81)
1.5 CaO	(79)			1.5 CaSiO ₃	(174)
16.6 C	(200)	8.3 CO	(232)	8.3 C	(100)

The essential reactions involved in the reduction are expressed by the reaction formula:



The heat requirements per ton of ore treated may therefore be figured out as:

			Calories.
Decomposition of	7.7ZnO	$= 84,800 \times 7.7$	$= 652,960$
"	2.7ZnSiO ³		
	into ZnO and SiO ²	$= 10,000 \times 2.7$	$= 27,000$
Decomposition of 0.6Fe ² O ³			
	into FeO and O	$= 64,200 \times 0.6$	$= 38,520$
Heat absorbed in decompositions			<u>$= 718,480$</u>
Formation of	1.2 FeSiO ³		
	from FeO and SiO ²	$= 8,900 \times 1.2$	$= 10,680$
Formation of	1.5 CaSiO ³		
	from CaO and SiO ²	$= 17,850 \times 1.5$	$= 26,770$
Formation of	8.3 CO	$= 29,160 \times 8.3$	$= 222,030$
Heat evolved in formation heats			<u>$259,480$</u>
Net heat of chemical reactions absorbed			<u>$459,000$</u>
Sensible heat in	7.7 Zn	$= 46,640 \times 7.7$	$= 359,130$
"	" 8.3 CO	$= 8,945 \times 8.3$	$= 74,240$
"	" 8.3 C	$= 5,760 \times 8.3$	$= 47,810$
"	" slag	$\left\{ \begin{array}{l} 1.2 \text{ FeSi}^1\text{O}^3 \\ 0.5 \text{ Al}^2\text{SiO}^5 \\ 1.5 \text{ CaSiO}^3 \end{array} \right.$	
		$= 413 \text{ kilograms} = 460 \times 413$	$= 200,000$
Sensible heat in products and residue			<u>$= 681,180$</u>
Add heat absorbed in chemical reactions			<u>$= 459,000$</u>
Total heat requirement of the charge			<u>$= 1,140,180$</u>

Important principle: The heat absorbed in an electric furnace by chemical reactions is electric energy utilized at an efficiency of 100 per cent. It is only part of the sensible heat of the materials being treated which is lost by radiation and conduction. Heat losses by radiation and conduction in electric furnace processes should be expressed upon the total energy of the current *diminished by the heat absorbed in chemical reactions*, and not upon the total energy of the current. This principle has been expressed most clearly by Mr. F. T. Snyder,

of Chicago, the pioneer electric furnace zinc metallurgist of America.

Expressed thus, electric furnaces give higher efficiencies the greater the absorption of heat in chemical reactions taking place within them. In mere physical processes, such as melting, electric furnaces on a large scale give 75 per cent net efficiency, with 25 per cent loss by radiation and conduction. In the above case, figured out for 1000 kg. of zinc ore, 40 per cent of the total heat requirement is absorbed as chemical heat at 100 per cent efficiency, and 60 per cent is needed as sensible heat. This 60 per cent then represents the net sensible heating effect, and the loss of heat by radiation and conduction must be calculated as one-third of this quantity, and not one-third of the total net heat requirement. We therefore have:

	Calories.
Net heat requirements for chemical reactions.....	459,000
“ “ “ “ “ sensible heat.....	681,180
Loss by radiation and conduction.....	227,060
Gross heat requirement of the furnace.....	1,367,240
Kilowatt hours of current required	

$$\frac{1,367,240}{860} = 1530$$

Mr. Gin's figures have been modified by the writer, as explained above, and anyone consulting his paper on this subject may make similar modifications to the other cases cited in that paper.

Mr. F. T. Snyder, of the Canada Zinc Company, at Vancouver, B. C., has operated the first practical electric zinc smelting furnace in America. Treating mixed lead and zinc ores, Mr. Snyder uses the furnace and process protected in his United States patents of July 2, 1907. (See *Electrochemical and Metallurgical Industry*, V. 323, 489.) The lead is obtained liquid, and the zinc also condensed to the liquid state before leaving the furnace proper, the heat of condensation being partly absorbed by water cooling the condensers and partly by the descending charges, which carry it back into the focus of the furnace. Under these circumstances, Mr. Snyder reports that he has attained unexpectedly low results as to

power requirement. It will be recalled, that in discussing the question of the electric smelting of zinc ores in general, and Mr. Gin's process in particular, we assumed the zinc vapor and CO gas to escape from the furnace at a minimum of 1033° C. If, as in Mr. Snyder's furnace, they escape at about 500°, the zinc liquid, the heat in these hot products is reduced very considerably, particularly that in the zinc. Mr. Snyder states in discussing Mr. Gin's paper (*loc. cit.*) that he has smelted pure zinc oxide at an expenditure of 1050 kilowatt hours per 1000 kilograms of oxide. Let us see how this coincides with the theoretical figures:

	Calories
Heat value of 1050 kw-hours.....	$= 1050 \times 860 = 903,000$
Heat of the chemical reactions, assumed to take place at ordinary temperatures.....	$1000 \times 687 = 687,000$
Sensible heat in products, at 500°	
Zinc: 800×80	$= 64,000$
CO: 342×152	$= 52,000$
	<hr/>
	$= 116,000$
Leaving, by difference for radiation, conduction and cooling water	$= 100,000$

Mr. Snyder does not give details as to the exact working of his furnace, but his claim to reduce a ton of zinc ore with 1000 kw-hours is seen to be a possibility, if he can remove the zinc as liquid zinc from the furnace, not lose too much heat in cooling water, and get most of the heat of condensation of the zinc vapor usefully returned by the descending charges into the working focus of the furnace.

Snyder's furnace, working as claimed, would show a useful efficiency of

$$\frac{803,000}{903,000} = 0.88 = 88 \text{ per cent.}$$

on the current used, with 12 per cent losses. The real heat losses, however, should be expressed upon the energy used less that absorbed in chemical reactions, or as 100,000 loss on 216,000 used for sensible heat,

$$\frac{100,000}{216,000} = 0.46 = 46 \text{ per cent.}$$

This shows that the furnace loses by radiation, conduction and cooling water 46 per cent of the energy developed as sensible heat in the furnace, but the latter item is only 24 per cent of the total energy applied to the furnace.

In short, about three-quarters of all the energy consumed by the furnace is utilized in the heat of the chemical reactions produced; of the other one quarter, half of it is represented by the sensible heat of the products leaving the furnace and half is lost by radiation, conduction and cooling water.

Zinc Vapor.

The condensation of zinc from the state of vapor follows the same laws as regulate the condensing of all gases. If it is by itself in a cooler space, it condenses by contact with the walls as finely divided zinc dust. (blue powder) if the walls are cold, as liquid zinc if the walls are hot, and it keeps on condensing until the tension of the remaining vapor is equal to the maximum tension of zinc vapor at the temperature of the condensing vessel. This condition having been reached, no more will condense until the condenser is cooled. At any temperature, therefore, an amount of zinc remains uncondensed corresponding to the maximum vapor tension of zinc at that temperature.

If other indifferent gases are present, the zinc vapor sustains only part of the atmospheric pressure, or pressure on the whole mixture, so that condensation cannot begin until a lower temperature is reached; that is, a temperature at which the maximum vapor tension of the zinc equals its partial vapor tension in the gas mixture. At this point condensation begins and continues as the temperature falls, the gas mixture always being saturated with zinc vapor. The phenomenon is precisely similar to the production of rain by the cooling of air containing moisture.

As to what the vapor tension of zinc is, the data are scanty. The boiling point under atmospheric pressure is 930°C. , where its vapor tension is 760 mm. of mercury column. According to Barus, the maximum tension increases 6.67 mm. for each 1°C. increase of temperature. This is a difficult determination, but corresponds satisfactorily with the calculated increase from analogy to water and mercury.

Water, boiling at 100°C. (373° absolute), varies 1° in boiling

point for 27.20 mm. variation in vapor tension; mercury, boiling at 357° C. (630° absolute) varies 1° in boiling point for 12.66 mm. variation in vapor tension. The ratio of the two variations is seen to be somewhere in the inverse ratio of the two boiling points.

$$\frac{630}{373} = 1.7$$

$$\frac{27.20}{12.66} = 2.2$$

If we compare mercury with zinc, with the two boiling points 357° and 930° (630° and 1203° absolute), and the observed variations in vapor tension at the normal boiling point of 12.66 mm. and 6.67 mm. per 1° rise in boiling temperature, the two ratios are

$$\frac{1203}{630} = 1.91$$

$$\frac{12.66}{6.67} = 1.90$$

This coincidence justifies us completely in assuming that the vapor tension curve of zinc may be calculated directly from that of mercury, by assigning for any given vapor tension an absolute temperature to the zinc vapor of 1.91 times that of mercury vapor. For cadmium we may use the similar ratio of the normal boiling points in absolute degrees:

$$\frac{273+780}{273+357} = \frac{1053}{630} = 1.67$$

and thus calculate the cadmium curve from the mercury curve.

From incipient vaporization to ebullition in a vacuum.

Tension of vapor mm. of Hg.	Mercury C°.	Cadmium C°.	Zinc C°.
0.0002	0	183	248
0.0005	10	200	267
0.0013	20	216	286
0.0029	30	233	305
0.0063	40	250	324
0.013	50	267	344
0.026	60	283	363
0.050	70	300	382

Tension of vapor mm. of Hg.	Mercury C°.	Cadmium C°.	Zinc C°.
0.093	80	317	401
0.165	90	333	420
0.285	100	350	439
0.478	110	367	458
0.779	120	383	477
1.24	130	400	496
1.93	140	417	516
2.93	150	433	535
4.38	160	450	554
6.41	170	467	573
9.23	180	483	592

Before proceeding further, we would remark that cadmium melts at 320° and zinc at 419°; that both can, therefore, show vaporizing phenomena nearly 150° below their melting points. At 9 mm. tension, 180° C., mercury begins to show the phenomena of ebullition, and we would, therefore, expect cadmium to "simmer" at 483° and zinc at 592°. Neither of these observations has as yet been experimentally investigated, so far as the author knows.

From ebullition in vacuum to normal boiling point.

Tension of vapor mm. of Hg.	Mercury C°.	Cadmium C°.	Zinc C°.
9.23	180	483	592
14.84	190	500	611
19.90	200	517	630
26.35	210	533	649
34.70	220	550	668
45.35	230	567	687
58.82	240	584	706
75.75	250	600	726
96.73	260	617	745
123.	270	634	764
155.	280	650	783
195.	290	667	802
242.	300	684	821
300.	310	700	840

Tension of vapor mm. of Hg.	Mercury C°.	Cadmium C°.	Zinc C°.
369.	320	717	859
451.	330	734	878
548.	340	750	897
663.	350	767	915
760.	357	780	930

The above table contains the more important data for the actual condensation of zinc, cadmium and mercury vapors in practice. Thus, if a mixture of zinc or cadmium vapor with an equal volume of indifferent gas goes into a condenser, the partial pressure of the metallic vapor being in this case only half an atmosphere, or 380 mm., no metal will commence to condense until the temperature of the gases is reduced to 862° for zinc and 720° for cadmium. If mercury vapor from a roaster is mixed with 19 times its volume of other gas, so that it only forms 5 per cent of the mixture, its partial tension will be only 5 per cent of 760 mm. = 38 mm., and no mercury will commence to condense until the temperature of the gas mixture is reduced to 224°. These temperatures are exactly analogous to the phenomenon of the dew point of moist air, the temperature at which rain forms.

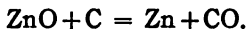
From normal boiling point to high pressures.

Tension of vapor atmospheres.	Mercury C°.	Cadmium C°.	Zinc C°.
1.0	357	780	930
2.1	400	851	1012
4.25	450	934	1107
8.	500	1018	1203
13.8	550	1101	1298
22.3	600	1185	1394
34.0	650	1268	1489
50.	700	1352	1585
72.	750	1435	1680
102.	800	1519	1776
137.5	850	1602	1871
162.	880	1652	1928

The latter table may have several special applications. If zinc, for instance, were placed in a closed electric furnace filled with indifferent gas and capable of supporting 100 atmospheres pressure, zinc could be kept in the liquid state up to some 1700° C., and its alloying with other metals greatly facilitated. In the making of brass, for instance, much zinc is lost by volatilization at the melting point of the copper used, yet a pressure on the furnace of four atmospheres would entirely prevent loss of zinc at the melting point of copper. Induction electric furnaces could easily be run inside a pressure vessel at this temperature, and the pressure be relieved gradually as the temperature of the melted alloy was reduced. To keep zinc from boiling, or to keep it in the liquid state, at 1300°, not a high temperature, would require a pressure of nearly 14 atmospheres to prevent it from boiling *ad libitum*.

Problem 135.

Roasted zinc sulphide ore, consisting practically of pure ZnO, is reduced by carbon, and the reduction gases passed into a condenser. Assume the reaction to be



Required:

(1) The temperature at which zinc commences to condense from the above gas mixture.

(2) The proportion of the zinc condensed out for each 1° reduction of temperature below this "dew point."

(3) The proportion of the zinc escaping uncondensed, if the gas escapes from the condenser at 600° C.

(4) How would these data be affected, if the reduction was taking place at Denver, 1500 meters above sea level, barometer 560 mm?

Solution:

(1) Since zinc vapor has been shown to have a specific gravity of 32.5 referred to hydrogen gas at the same temperature and pressure, and the molecular weight of hydrogen gas, formula H_2 , is 2, the molecular weight of zinc vapor must be $2 \times 32.5 = 65$. This coincides with the atomic weight of zinc, and therefore zinc vapor is monatomic and the symbol of its molecule is Zn. The gas mixture in the above equation con-

tains, therefore, one molecule each of its constituents, and, therefore, each gas supports half the atmospheric pressure. This is ordinarily expressed by saying that the gas is half one constituent and half the other, meaning that if the two gases were separated and each measured under the prevailing normal pressure, the volume of each would be half the volume of the gas mixture. The statement that each supports half the normal pressure is the more scientific and logical, for in a gas mixture each gas certainly possesses the volume of the mixture, but under only a fraction of the pressure on the mixture, said fraction being identical with the fraction of the volume of the whole which it would constitute, if measured separately under the pressure supported by the mixture.

Consulting the table, we find zinc vapor to have a pressure of 380 mm. at 862° . This would, therefore, be the dew point, at which the zinc would commence to condense. (1)

(2) At this condensing temperature, a difference of 19° in the temperature corresponds to 82 mm. difference in the maximum vapor tension, and, therefore, in this gas mixture at this temperature, a reduction of 1° in its temperature will reduce the tension of the zinc vapor $82 \div 19 = 4.3$, or practically 4 mm.

This will result in the condensation of $\frac{4}{380}$ th. of the zinc, because its tension was 380 and was reduced to 376, and, therefore, $\frac{376}{380}$ th. of it remained uncondensed. The proportion condensed for the reduction of 1° in temperature is, therefore, a

trifle over 1 per cent. (2)

(3) Leaving the condenser at 600° , the tension of the zinc vapor escaping would be, from the table, 11.6 mm. The tension of the CO gas would, therefore, be $760 - 11.6 = 748.4$ mm. For every cubic meter of mixed gases, at 862° , containing a cubic meter of zinc vapor at that temperature and 380 mm. pressure, there will escape a fraction of a cubic meter of mixed gas at 600° , containing zinc vapor at 11.6 mm. pressure. The fractional volume can be calculated from the tension on the CO.

1 m³ CO at 862° and 380 mm. pressure, reduced to 600° and 748.4 mm. pressure, becomes

$$1 \times \frac{600+273}{862+273} \times \frac{380}{748.4} = 0.381 \text{ m}^3.$$

This is, then, the actual volume of gas mixture escaping, for each actual 1 m³ of gas mixture in the condenser at the "dew point," 862°.

The uncondensed zinc vapor is, therefore, 0.381 m³ at 600° and 11.6 mm. tension. This would be, at 862° and 380 mm. tension

$$0.381 \times \frac{862+273}{600+273} \times \frac{11.6}{380} = 0.015 \text{ m}^3.$$

There, therefore, escaped uncondensed

$$\frac{0.015}{1.000} = 0.015 = 1.5 \text{ per cent of the zinc.} \quad (3)$$

A quicker solution, not so easy to understand, however, is

$$\frac{11.6}{748.4} = 0.015 = 1.5 \text{ per cent uncondensed.}$$

(4) If the operation takes place at such elevation above sea-level that the barometer stands normally at 560 mm., then the partial pressure of the zinc vapor in above case would be 280 mm. instead of 380 mm. and the "dew point" or temperature at which condensation commences would be 835° instead of 862°, as under previous conditions.

At this temperature, a difference of 1° in the temperature corresponds to a difference of 3 mm. in the tension of the zinc vapor, producing therefore a condensation of the zinc present, per 1° fall of temperature, of $3 \div 280 = 0.011 = 1.1$ per cent, instead of 1.2 per cent.

If the temperature of the escaping gases is 600°, with the saturated zinc vapor at 11.8 mm. tension and the carbonous oxide, CO, at $560 - 11.8 = 548.2$ mm., the proportion of the original quantity of zinc escaping uncondensed is $11.8 \div 548.2 = 0.022 = 2.2$ per cent, instead of 1.5 per cent.

Condensation of Zinc and Mercury Vapors.

The temperature at which a metallic vapor, like zinc or mercury, commences to condense, depends upon the vapor tension curve of the metal and the amount of other uncondensable gas

with which it is mixed. These intermixed gases reduce the pressure upon the metallic vapor, and lower the temperature at which the vapor becomes saturated vapor. The phenomenon is exactly analogous to the "dew point" of air and the precipitation of rain.

Problem 136.

A roasted zinc ore contains 15 per cent. Fe^2O^3 and 70 per cent. Zn O. It is reduced by excess of carbon, in a retort.

Required:

- (1) The average composition, by volume, of the gas mixture entering the condenser, assuming no CO^2 in it.
- (2) The "dew point" of the mixture at which it begins to deposit zinc.
- (3) The percentage of zinc escaping condensation, if the gases leave the condenser at 600°C .

Solution:

(1) Per kilogram of zinc there is used, assuming complete reduction:

$$1 \div (0.70 \times 65/81) = 1.78 \text{ kg.}$$

Oxygen in 1.78 kg. of ore:

$$\begin{aligned} \text{As Zn O} &= 1 \times 16/65 = 0.246 \text{ kg.} \\ \text{As Fe}^2\text{O}^3 &= 1.78 \times 0.15 \times 48/160 = 0.080 \text{ "} \\ \text{Sum} &= 0.326 \text{ "} \end{aligned}$$

$$\text{Co formed} = 0.326 \times 28/16 = 0.57 \text{ "}$$

$$\text{Volume of CO} = 0.57 \div 1.26 = 0.45 \text{ m}^3$$

$$\text{Volume of Zn} = 1.00 \div 2.93 = 0.34 \text{ m}^3$$

$$\text{Sum} = 0.79 \text{ m}^3$$

Percentage composition of gases:

$$\text{CO} = 57 \text{ per cent.}$$

$$\text{Zn} = 43 \text{ " (1)}$$

(2) If the barometric pressure is assumed normal, then the zinc vapor supports

$$760 \times 0.43 = 327 \text{ mm}$$

and the temperature at which the mixture becomes saturated with zinc vapor is found from the table on page 620 to be 847° .

This is 83° below the normal boiling point of zinc.

(3) From 847° down, the vapor in the retort will be always saturated, its tension being found from the tables. The proportion of original zinc condensed, or remaining uncondensed, cannot be inferred simply from the vapor tension at any temperature. For instance, the vapor tension of the zinc at 600° C. is 12 mm of mercury column. The CO gas leaving the condenser at this temperature will, therefore, be at a tension of $760 - 12 = 748$ mm, and will be accompanied by $12/748$ of its volume of zinc vapor; as it came into the condenser it was accompanied by $327/433$ of its volume of zinc vapor. The ratio of these two quantities or proportions represents the real fraction of the zinc escaping uncondensed; that is, the proportion escaping condensation, in terms of the total zinc concerned, is

$$12/748 \div 327/423 = 0.016 \div 0.773 = 0.008 = 0.8 \text{ per cent.}$$

The same result can be calculated in several ways. One is based on the datum that at any given temperature zinc vapor is $65 \div 28 = 2.3$ times as heavy as CO gas.

Problem 137.

Numerous attempts have been made to reduce Zn O continuously in a blast furnace, and condense the zinc from the gases. In such a case, the gases will consist of zinc vapor, carbon monoxide and nitrogen, and the deficit of reduction heat must be obtained by the burning of carbon to CO at the region of the tuyeres. A low charge column must be used in order that the gases pass out hot enough to carry the zinc. Assume the gases to escape at 900° C., and the furnace to lose by radiation and conduction, etc., an amount of heat equal to the sensible heat in the blast used.

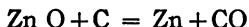
Required:

- (1) The amount of fixed carbon to be charged into the furnace, per 2000 lb. of zinc.
- (2) The composition of the gases leaving the furnace.
- (3) The temperature at which these gases will begin to deposit zinc or become saturated with zinc vapor.
- (4) The proportion of the zinc they carry which will escape from the condensers, as vapor, at 600° C.
- (5) The pressure necessary to apply to the furnace to keep

the zinc in the melted state at the minimum temperature of reduction, 1033° C.

Solution:

(1) If the reaction is assumed as practically



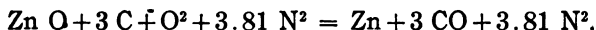
there is needed for reduction, per 2000 lb. of zinc

$$2000 \times (12/65) = 369 \text{ lb.}$$

There is in this reaction a deficit of heat, which is per 65 parts of zinc concerned simply

$$(\text{Zn, O}) - (\text{C, O}) = 84,800 - 29,160 = 55,640.$$

This deficit can only be made up by burning more C to CO right at the tuyeres. If two more atoms of carbon were burned we would have a little more than enough heat. We will, therefore, assume the reaction at the tuyere region as the using of one atom of carbon for reduction and of double as much for supplying the heat deficit, and since one volume of oxygen is accompanied by 3.81 volumes of nitrogen, the whole reaction will be



The amount of fixed carbon necessary is approximately three times that necessary for reduction only and amounts, per 2000 lb. of zinc, to

$$36 \times \frac{2000}{65} = 1108 \text{ lb.} \quad (1)$$

(2) The furnace gases, therefore, contain, by volume,

Zinc vapor	= 1	volume = 12.8 per cent.
Carbon monoxide	= 3	" = 38.4 "
Nitrogen	= 3.81	" = 48.8 " (2)

(3) The gases will be saturated with zinc vapor when the partial pressure of the zinc, which is

$$760 \times 0.128 = 97 \text{ mm}$$

is equal to the maximum tension of zinc at the temperature attained. This is at 745° C., as seen from inspecting the vapor tension tables, or 185° below the normal boiling point of zinc. (3)

(4) The relative volume of zinc vapor to uncondensable gas in the original gases is

$$\frac{12.8}{87.2} = 0.147$$

In the gases issuing from the condenser at 600° it would be

$$\frac{12.0}{748} = 0.016$$

The proportion of the zinc escaping condensation under these conditions would, therefore, be

$$\frac{0.016}{0.147} = 0.109 = 10.9 \text{ per cent.} \quad (4)$$

By cooling the gases to the melting point of zinc, it would be possible to leave uncondensed only

$$\frac{0.165}{759.8} \div 0.147 = 0.0014 = 0.14 \text{ per cent.}$$

(5) If it was a question only of keeping pure zinc from vaporizing at 1033°, in the absence of other gases, we could at once consult the vapor tension table, and find 2.2 atmospheres as the actual tension of zinc vapor at 1033°, corresponding to 1.2 atmospheres effective pressure upon the furnace. But in the gas mixture coming from the furnace the zinc is practically one-eighth, by volume, of the gases, which means that it sustains one-eighth of the pressure upon the whole. It would, therefore, take a tension of

$$2.2 \times 8 = 17.6 \text{ atmospheres}$$

to keep all this zinc in the liquid state, corresponding to an effective pressure of 16.6 atmospheres. (5)

This is an entirely impracticable working condition and shows the practical impossibility of the schemes upon which much money have been spent for reducing zinc ore to liquid zinc in a blast furnace run under high pressure.

Problem 138.

In the metallurgy of mercury, the average ore contains 2 per cent. of Hg S and is roasted by the use of 10 per cent. of its

$$\begin{array}{rcl}
 \text{Hg} & 760 \times 0.005 = & 3.8 \text{ mm} \\
 \text{SO}^2 & 760 \times 0.005 = & 3.8 \text{ " } \\
 \text{H}^2\text{O} & 760 \times 0.221 = & 168.0 \text{ " } \\
 \text{N}^2 & 760 \times 0.613 = & 465.9 \text{ " } \\
 \text{CO}^2 & 760 \times 0.156 = & 118.5 \text{ " } \\
 & \hline
 & & 760. \text{ " }
 \end{array}$$

The mercury will, therefore, commence to condense when the temperature of the gas mixture is that of mercury vapor at a maximum tension of 3.80 mm. From the vapor tension table of mercury we find this to be 156° C., or 201° below the normal boiling point of mercury. Above this temperature the gas mixture is not saturated with Hg vapor and no condensation can occur. (2)

(3) In the gas mixture, the mercury vapor is equivalent to 3.8/760 of the volume of the whole, or 3.8/756.2 of the volume of the other gases. This latter proportion is 0.00503. At 100° C., the uncondensed mercury vapor can have a tension of 0.285 mm, leaving 759.715 to the other gases, and giving the ratio of mercury vapor to other gases 0.000375. Since the other gases have remained constant in amount, the proportion of mercury remaining condensed is

$$0.000375 \div 0.00503 = 0.075 = 7.5 \text{ per cent.}$$

If the temperature of the mixture is reduced to 50° C., the mercury vapor remaining can exert a tension of only 0.013 mm and the water vapor only 92 mm. The other gases present will therefore sustain $760 - (92 + 0.013) = 668$ mm. In the original mixture the Hg and H²O vapors are, respectively, equivalent to

$$\begin{array}{rcl}
 \text{Hg} & 3.8 \div 587.2 = & 0.0065 \\
 \text{H}^2\text{O} & 168.0 \div 587.2 = & 0.2860
 \end{array}$$

of the volume of N², CO² and SO² together.

In the gas escaping at 50° the Hg and H²O will be equivalent to

$$\begin{array}{rcl}
 \text{Hg} & 0.013 \div 668 = & 0.00002 \\
 \text{H}^2\text{O} & 92. \div 668 = & 0.1377
 \end{array}$$

of the volume of the same gases.

The proportions of the Hg and H²O escaping uncondensed at 50° will, therefore, be

$$\text{Hg } 0.00002 \div 0.0065 = 0.0031 = 0.31 \text{ per cent.}$$

$$\text{H}^2\text{O } 0.1377 \div 0.2860 = 0.4815 = 48.15 \text{ per cent.}$$

By exactly similar reasoning, using the maximum tensions of Hg and H²O at 15° (0.0009 mm and 13 mm, respectively), the proportions of each to the N² + CO² + SO² are

$$\text{Hg } 0.0009 \div 747 = 0.0000012$$

$$\text{H}^2\text{O } 13. \div 747 = 0.0174$$

and the proportions escaping condensation would be

$$\text{Hg } 0.0000012 \div 0.0065 = 0.00018 = 0.018 \text{ per cent.}$$

$$\text{H}^2\text{O } 0.0174 \div 0.2860 = 0.06064 = 6.064 \text{ per cent. } (4)$$

The differences between these percentages and 100 will be the proportions of these materials condensed to the liquid state.

METALLIC MIST OR FUME.

When zinc or mercury are in the state of vapor their atoms are each separate from other atoms. Chemically speaking, their vapor molecules are mon-atomic. On condensing to the liquid state we do not know whether the atoms come together into compound molecules or whether they simply come closer together. In either case, the molecules of the liquid metal, as the temperature is reduced low enough to form them, exist at first as isolated molecules, constituting the liquid metal in its finest possible state of sub-division, so small that it is for the time being practically still a gas. If, however, we give these liquid molecules the possibility of uniting to liquid masses, we get the latter. This is a matter principally of reducing the surface tension which holds the liquid molecules each to itself as a sphere. Contact with a rubbing surface, with dust particles, filtration through cloth, or even electrification (perhaps a magnetic field) reduce this surface tension and cause agglomeration into liquid masses which precipitate.

The amount of liquid or solid particles thus held in suspension and escaping with the current of uncondensable gas is entirely independent of the quantity escaping as true vapor, which has been calculated above, except in so far as they are both functions of the amount of said uncondensable gas. The velocity of the escaping current is a large factor in the amount of mist, because the carrying power of gas for mist particles varies

probably with the cube of its velocity, so that halving the velocity of the issuing gas will diminish greatly this source of loss. Large settling chambers in which the mist can deposit, because of stagnation of the gas current, and large rubbing surfaces, are effective means for catching or depositing the mist. Filtration through bags is still more effective.

In the case of zinc, the solidifying point is 420° , while condensation from the state of vapor begins at, say, 860° . In this interval only can the condensed particles, as a mist, collect together to liquid zinc. If the temperature passes quickly through this range, the particles have little chance to agglomerate into liquid masses, and the proportion which chills into solidified mist particles is increased. These solidified mist particles, analogous to "hoar frost" in nature, form the well known "blue powder" of the zinc works. It settles in large settling chambers, and is in extremely fine particles, mostly under 0.01 mm in size. It is quite easy to collect all the zinc in this form if the vapor is chilled suddenly and the resulting gas settled properly or filtered.

The loss of mercury or zinc as mist or hoar frost is therefore, to be considered entirely apart from the loss as true vapor; it may be smaller than the latter and it may be larger; its amount varies particularly with the nature of the settling apparatus and the velocity of the gases as they escape. The theory as to its amount under any given set of conditions would be very difficult to elaborate, and the data for doing so with exactness are practically unknown. The best that can be done at present is to study the loss as mist or hoar frost in actual practice, experimentally, and tabulate the actual results as a guide for future metallurgical use.

CHAPTER V.

METALLURGY OF ALUMINIUM.

The two essential principles here involved are "differential reduction" as used in the electric furnace purification of alumina, and "electrolytic furnace operation," as illustrated in the decomposition of the alumina by electrolysis in the manner usually practiced. Only the latter problem will be covered here.

ELECTROLYTIC FURNACE REDUCTION OF ALUMINA.

The Hall process is beautifully simple and technically admirable. Al^2O^3 is found to dissolve in melted alkaline-aluminium double fluorides; it is as pretty a case of solution, so far as appearances go, as dissolving a spoonful of powdered sugar in a glass of distilled water. The melting point of the fused fluorides is reduced by the solution of alumina, just as that of water is reduced by dissolving salt. In passing the electric current the constituents of the dissolved alumina appear at the electrodes, oxygen at the anode and aluminium at the cathode. The best practical arrangement is to use a carbon-lined pot, with molten aluminium in the bottom as the cathode, upon it a few inches depth of the bath, and dipping into this the carbon anodes. The writer has given most of the technical details of this operation in his treatise on "Aluminium," and Prof. Haber has published extensive laboratory studies of the process in the *Zeitschrift für Elektrochemie*.

With a solvent salt consisting of melted sodium fluoride and aluminium fluoride, such as called for in one of the Hall patents, with alumina dissolved therein, and using carbon anodes, the electrolytic elements of the process are simplicity itself. The bath contains sodium, aluminium, fluorine and oxygen, and the anode is carbon. Under these conditions those elements or compounds will form at the electrodes which cannot further react upon the bath material; in other words, those materials most stable in contact with the bath material or electrodes. A mo-

ment's reflection explains what happens, and what must happen. At the cathode, sodium cannot be liberated because metallic sodium reacts chemically on this bath, separating out aluminium; therefore, the electrolytic reducing tendency at the surface of the cathode can only expend itself in separating out aluminium. At the anode, fluorine cannot be liberated because fluorine acts strongly upon alumina even when cold, converting it into fluoride and expelling its oxygen; therefore, the electrolytic perducing tendency at the surface of the anode will tend to set free oxygen. But oxygen cannot be set free at a carbon surface at a cherry-red heat because of its inevitable tendency to unite with the carbon to form CO. The electrolytic agency at the surface of the carbon anode must, therefore, cause the formation of CO. The whole electrolytic operation results in the removal of Al^{2}O^3 from the bath and the formation of aluminium and carbon monoxide.

The thermochemical relations, as far as known, agree absolutely with the above explained experimental results. The materials in presence of each other are sodium fluoride, aluminium fluoride, aluminium oxide and carbon. The heats of formation of these, per molecule and per chemical equivalent concerned, are as follows:

(Na, F)	= 109,720	= 109,720	per chemical equivalent.
(Al, F ³)	= 275,220	= 91,740	" " "
(Al ² , O ³)	= 392,600	= 65,430	" " "
(C, O)	= 29,160	= 14,580	" " "

The heat of formation of carbon tetra-fluoride is unknown, but is probably small, since it is so difficult to form.

From the last column, which largely governs the work done by the current, we see that the current does far the least work when it decomposes alumina; in fact, it does still less, by 14,580 calories, because of the assistance rendered by carbon uniting with the oxygen. Now, although the electrical current does not consistently adhere to the doctrine of "least work," yet it does in this case because forced to do so by the chemical relations of sodium, aluminium, fluorine, oxygen and carbon at the temperature of the bath, as explained in the preceding analysis. It is probable that in electrolysis the chemical relations of the possible products control what the current does rather than the

thermochemical relations alone, but in most cases the two conditions or controlling circumstances coincide in their influence and lead to identical results. This is the case in the process in question; it is absolutely normal and is explainable by either method of reasoning.

If the operation is run with a small vessel and correspondingly small current, the heat necessarily evolved by the passage of the current is small compared to the conduction and radiation losses and must be supplemented by outside heating to keep the contents at proper temperature. If the size of the operation is increased in all its items and dimensions, the necessarily generated internal "resistance" heat will suffice to keep the bath at the requisite temperature, when the enlargement is done on a certain scale. If enlarged past this point, too much internal heat is unavoidably generated and means must be used to artificially cool the pot.

Problem 139.

An electrolytic vessel is composed of a block of carbon 25 cm cube, with a cavity 10 cm square by 10 cm deep inside. The cavity has a round carbon, 5 cm diameter, dipping into it. The vessel weighs 30 kilograms; the fused bath in the cavity 2 kg; the carbon immersed in it 0.1 kg. The specific heat of the carbon is 0.5, of the bath 0.3, at the running temperature. An experiment showed that the bath material cooled off, at the working temperature, at the rate of 10° C. per minute, the walls of the vessel at an average rate of 2° C. per minute, when left to cool by themselves.

Required:

- (1) The number of watts which must be converted into heat in the vessel in order to maintain it at the working temperature.
- (2) Assuming 75 per cent. of the theoretical ampere efficiency to be obtained, what amperes passed through the pot will keep it at working temperature if the working voltage is kept at 10 volts?

Solution:

- (1) The 30 kg of vessel material losing heat at the rate of 2° per minute, with specific heat of 0.5, gives a heat loss per minute of

$$30 \times 0.5 \times 2 = 30 \text{ Calories.}$$

Similarly, the immersed carbon in the cavity and the bath material itself lose

$$0.1 \times 0.5 \times 10 = 0.5 \text{ Calories.}$$

$$2.0 \times 0.3 \times 10 = 6.0 \quad "$$

The total heat loss is, therefore, 36.5 Calories per minute.

To maintain the temperature constant the current must furnish this heat, and since 1 watt is 0.239 gram calories per second, the watt energy thus converted into heat must be

$$\frac{36.5 \times 1000}{0.239 \times 60} = \mathbf{2545} \text{ watts} \quad (1)$$

(2) If all the amperes passing through, separated out metal the voltage absorbed in decomposition in the bath would be from the thermochemical heats of formation of chemical equivalent quantities of $\text{Al}^3 \text{O}^3$ and CO :

$$\frac{65,430 - 14,580}{23,040} = \mathbf{2.2} \text{ volts.}$$

If 75 per cent. of the amperes are efficient, the voltage thus absorbed is

$$2.2 \times 0.75 = 1.65 \text{ volts.}$$

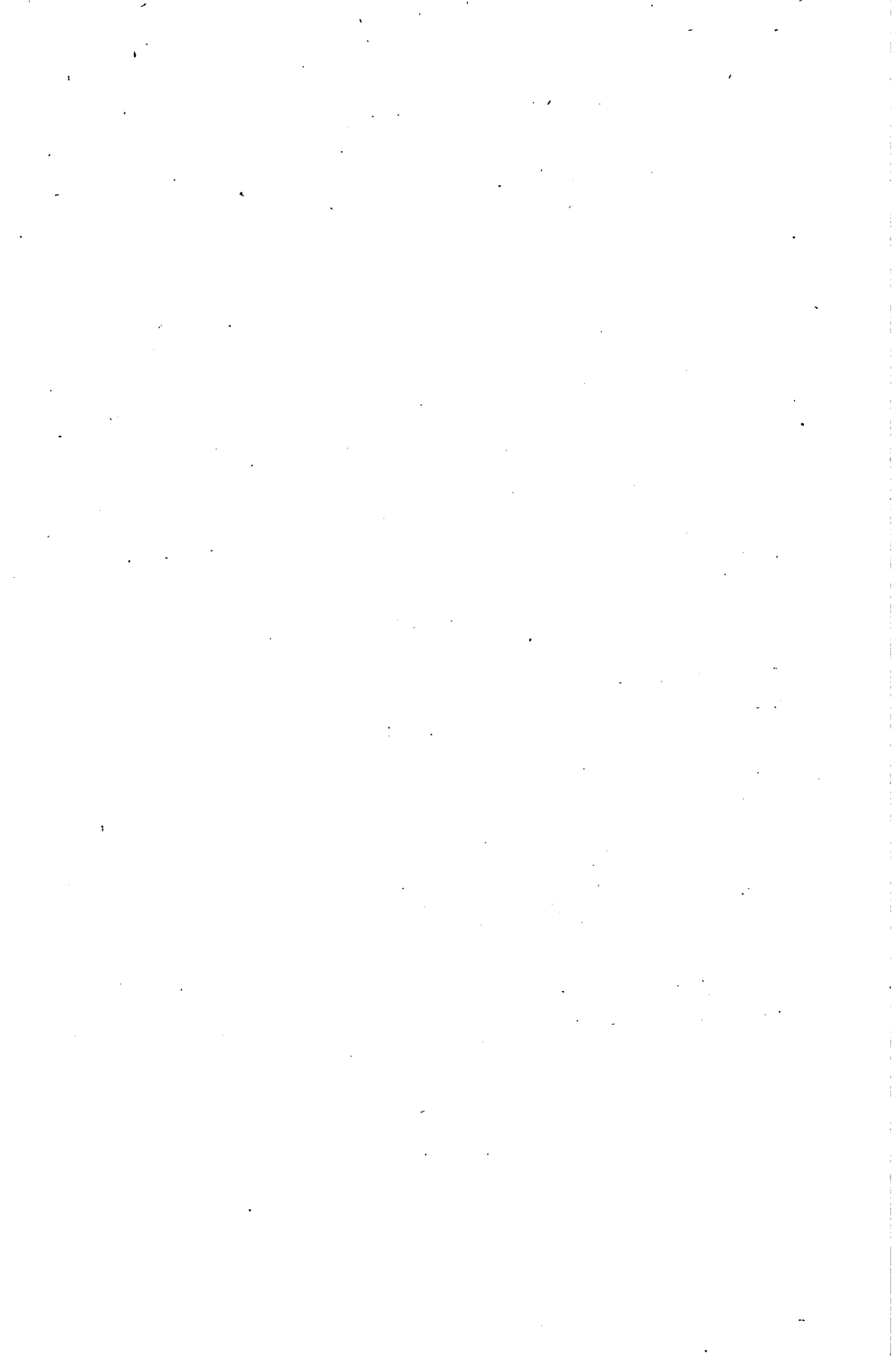
The voltage disappearing in overcoming ohmic resistance will then be

$$10 - 1.65 = 8.35 \text{ volts}$$

and the current which when passed will keep the pot at working temperature will be

$$\frac{2545}{8.35} = \mathbf{305} \text{ amperes.} \quad (2)$$

The above-used principles are applicable to any kind of electrolytic-furnace operation.



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